

# IDEM

## Nonrule Policy Document

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**Brief Description of Subject Matter:** The sample collection techniques described in Methods 5021 and 5035 represent a significant departure from those traditionally used in the environmental arena to sample soils for volatile organic compounds (VOCs). The new techniques were developed because the traditional methods of collection, handling, transportation, and storage did not effectively reduce VOC losses attributable to volatilization and microbial action. This resulted in reported concentrations of VOCs in soil being significantly underestimated.

While the intention being the new methods was to improve accuracy, facilities, consultants, and laboratories found them difficult to implement. They included confusing language and impractical requirements. Since Methods 5035 and 5021 were published, additional studies have been performed that improve upon the procedures originally presented and render them more practical. Indiana Modified Method 5035 (IN 5035-M) is an adaptation of SW-846 Method 5035 that takes these newer findings into account, providing increased accuracy and clarity of instruction.

This nonrule policy document is intended solely as guidance and does not have the effect of law or represent formal Indiana Department of Environmental Management (IDEM) decisions or final actions. This nonrule policy document shall be used in conjunction with applicable laws. It does not replace applicable laws, and if it conflicts with these laws, the laws shall control. A revision to this nonrule policy document may be put into effect by IDEM once the revised nonrule policy document is made available for public inspection and copying. IDEM will submit revisions to the Indiana Register for publication.

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## INDIANA MODIFIED METHOD 5035

### **MODIFIED METHOD FOR THE SAMPLING, HANDLING, AND STORAGE OF SOILS AND WASTES TO BE ANALYZED FOR VOLATILE ORGANICS**

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## INDIANA MODIFIED METHOD 5035

### **MODIFIED METHOD FOR THE SAMPLING, HANDLING, AND STORAGE OF SOILS AND WASTES TO BE ANALYZED FOR VOLATILE ORGANICS**

#### 1.0 SCOPE AND APPLICATION

- 1.1 This method provides guidance for the collection, storage, and preparation of solid samples (soils, sediments, and solid waste) for the analysis of volatile organic compounds (VOCs). A process is described that minimizes pre-analysis sample transfer and eliminates laboratory subsampling prior to purge-and-trap introduction to a gas chromatograph (GC) or gas chromatograph/mass spectrometer (GC/MS) for analysis. Minimal exposure of the sample to the atmosphere reduces losses of VOCs from volatilization and microbial action that would otherwise occur during sample transport, handling, and analysis.
- 1.2 Three options are presented for the collection, preservation, and storage of samples collected for environmental projects in the state of Indiana: two default options and a Performance Based Measurement System (PBMS) approach. Options 1 and 2, the default options, involve collection of a small soil plugs with coring devices followed by transfer to a VOA vial. Each default option results in an intact sample core in a hermetically sealed autosampler vial following a single transfer from sampling device to vial. They include:
  - 1.2.1 Option 1: Collection and transportation in coring devices with airtight sample chambers with transfer to autosampler vials at the laboratory.  
*Option 1 is summarized in section 2.1 of this guidance. Sample container preparation is discussed in section 6.1.1. Detailed instructions for Option 1 are provided in section 6.2.1.1.*
  - 1.2.2 Option 2: Transfer from coring device to empty VOA vial in the field, using the empty VOA vial for sample transportation and storage.  
*Option 2 is summarized in section 2.2 of this guidance. Sample container preparation instructions are found in section 6.1.2. Detailed instructions for Option 2 are provided in section 6.2.1.2.*
- 1.3 Option 3: A Performance Based Measurement System (PBMS) approach is available as a third option. The PBMS option allows use of alternate procedures if an adequate demonstration is made that data quality is not compromised by the modifications or substitutions. "Adequate demonstration" requires thorough documentation.  
*Option 3 is discussed in section 2.3 of this guidance.*
- 1.4 Multiple aliquots are collected from each sampling point (including each depth for subsurface borings) to allow for initial screening, determinative analysis, and reanalysis (when necessary) without jeopardizing sample integrity and data quality. The multiple collocated aliquots also allow for dry weight determination.

- 1.5 Dry weight determination must be performed, and results must be reported on a dry weight basis, on all (high level and low level) samples that are being analyzed for *remediation-related projects*.

*Instructions for dry weight determination are provided in section 7.5 of this guidance. The instructions apply to both low level and high level samples.*

1.5.1 Results **must be reported** on a dry weight basis for samples being analyzed for the following types of projects:

- Site assessments (of any type, for any program);
- Risk assessments (of any type, for any program);
- Resource Conservation and Recovery Act (RCRA) closures;
- RCRA Corrective Action projects;
- Voluntary Remediation Plan (VRP) projects;
- State Cleanup projects;
- Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or “Superfund”) projects;
- Leaking Underground Storage Tank (LUST) projects; and
- Enforcement-driven cleanups.

- 1.6 Dry weight determination must also be performed on high level samples being characterized for *disposal purposes* that will be extracted in methanol. However, wastes being characterized for disposal should not be reported on a dry weight basis. In this case the dry weight determination is used to find out the amount of water in the sample. This water will be extracted by the methanol along with the analytes of interest. The dry weight information provides a tool to assess the dilution effects this water has on surrogates and internal standards.

*Instructions for dry weight determination are provided in section 7.5 of this guidance.*

It is not necessary to perform a dry weight determination on low level samples being characterized for disposal purposes.

1.6.1 Results **should not be reported** on a dry weight basis for the following types of samples, even if dry weight is determined:

- Excavated soils and sediments being characterized for disposal,
- Other special wastes and solid wastes being analyzed for waste classification,
- Other special wastes and solid wastes being characterized for disposal.

- 1.7 Sample preparation and introduction procedures are dependent on the approximate concentration range of VOCs in the samples: low level or high level.

1.7.1 Low level samples: The applicable concentration range for low level soils is dependent on the determinative method, matrix, and compound. The VOC concentrations of low level samples will generally fall in the range of 0.5 to 200 µg/kg. The actual upper concentration limit will correspond to the high end of the linear range of the low level calibration curve. Sample collection,

preparation, and introduction procedures for low level samples are outlined in this method.

- 1.7.2 High level samples are those with VOC concentrations exceeding the calibration range for low level soils (generally >200 Fg/kg). Oily wastes are always treated as high concentration samples. Sample collection and preparation of high concentration and oily materials are performed using the procedures described in this method. However, sample introduction of high level samples is performed after methanol extraction or waste dilution using the aqueous purge-and-trap procedure in SW-846 Method 5030 or by the equilibrium headspace analysis procedure in SW-846 Method 5021.
- 1.8 Indiana Modified Method 5035 (IN 5035-M) procedures can be used for most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile, water-soluble compounds can also be sampled and prepared by these techniques. However, GC or GC/MS quantitation limits will be approximately ten times higher than those for insoluble compounds because of poor purging efficiency.
- 1.9 Indiana Modified Method 5035 procedures may be used in conjunction with any appropriate determinative gas chromatographic or GC/MS procedure. Examples of such procedures include SW-846 Methods 8015, 8021, and 8260. IN 5035-M must be used by or under the supervision of trained samplers and analysts. Analysts must demonstrate the ability to generate acceptable results for this preparation method in combination with a given determinative chromatographic procedure prior to submittal of such data.
- 1.10 IN 5035-M is modeled on and borrows heavily from USEPA SW-846 Method 5035, "Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples" (Revision 0, December 1996). Modifications are based on the following documents, in addition to considerations and concerns specific to Indiana:
- 1.10.1 Attachment 2 of the USEPA Office of Solid Waste memo, "Clarification Regarding Use of SW-846 Methods,"<sup>1</sup> (hereinafter referred to as "EPA Clarification Memo");
- 1.10.2 ASTM Method D4547-98, *Standard Guide for Sampling Waste and Soils for Volatile Organic Compounds*<sup>2</sup>;

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<sup>1</sup>Memorandum to RCRA Senior Policy Analysts Region I-X, from Elizabeth Cotsworth, Environmental Protection Agency, Acting Director, Office of Solid Waste, "Clarification Regarding Use of SW-846 Methods" (Washington, D.C.: U.S. EPA, August 7, 1998), photocopy, Attachment 2, 3-6.

<sup>2</sup>American Society for Testing and Materials (ASTM) Committee D-34 on Waste Management, Subcommittee D34.01 on Sampling and Monitoring, ASTM D-4547-98, *Storage and Preservation of Soil Samples for Volatile Organic Compound Analysis* (West Conshohocken, PA: ASTM, November 1998), photocopy.

1.10.3 CRREL Special Report, *Storage and Preservation of Soil Samples for Volatile Organic Compound Analysis*<sup>3</sup>; and

1.10.4 En Novative Technologies, Inc. Report, *Report on Method 5035 and En Core Hold Times*.<sup>4</sup>

## 2.0 SUMMARY OF METHOD

Two options are presented for the collection, transportation, and storage of soil samples to be analyzed for VOCs in the state of Indiana. Each option results in an intact sample core in a hermetically sealed autosampler (VOA) vial following a single transfer from sampling device to vial. Vials used must be appropriate for the sample introduction method and instrumentation used at the analyzing laboratory.

A Performance Based Measurement System (PBMS) approach is available as a third option. The PBMS option allows use of alternate procedures providing an adequate demonstration that data quality is not compromised by the modifications or substitutions. Election of the PBMS approach requires pre-approval by IDEM.

**Notes:** (1) **The collection of bulk samples (e.g., in large bottles or traditional wide mouth 4-oz. VOA jars) that would require laboratory subsampling is not an option under IN 5035-M except as a PBMS approach.** In addition, IDEM will not approve PBMS proposals for collection of bulk soil samples unless samples are known to contain high VOC concentrations (exceeding the linear range of low level calibration curve) and benzene is not a contaminant of concern.

(1) **Preservation/extraction of samples with methanol is generally not appropriate for low concentration samples.** If presented as a PBMS approach, documentation must be provided demonstrating that the detection limits required by the project objective can be reached for **all** analytes of concern.

### 2.1 Option 1: Collection and Transportation of Intact Sample Plugs in Coring Devices with Airtight Storage Chambers

In this option, multi functional devices designed to operate both as coring tools and airtight storage containers are used. The device collects a small sample core directly into a volumetric storage chamber, filling it completely with zero headspace. The storage

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<sup>3</sup>U.S. Army Corps of Engineers, Cold Regions Research & Engineering Laboratory, *Storage and Preservation of Soil Samples for Volatile Organic Compound Analysis*, CRREL Special Report 99-5 by Alan D. Hewitt (Hanover, NH: USACE CRREL, May 1999).

<sup>4</sup>David Turriff and Chris Reitmeyer, *Validation of Holding Times for the En Core™ Sampler* (Green Bay, WI: En Novative Technologies, August 1998).

chamber is then capped, forming an airtight seal and cooled to approximately 4EC.<sup>5</sup> The intact samples are transported to the laboratory in the sealed devices.

2.1.1 Option 1a - Collection and Transportation in Coring Devices with Airtight Sample Chambers: Receipt at Laboratory Within 2 Calendar Days of Sampling; Analysis Within 1 Additional Calendar Day.

To allow for concentration range screening, dry weight determination, determinative analysis, and reanalysis (when necessary), multiple collocated aliquots (collocated samples in multiple coring/storage devices) are collected from each sampling location and depth, sealed, and stored on ice in a cooler. The cooler is kept chilled at approximately 4EC and shipped with plenty of ice to the laboratory for receipt within 2 calendar days of sampling.

The chain-of-custody form is checked and signed; the samples are logged in; and the laboratory extrudes, prepares, and analyzes samples as soon as possible on the day of receipt. Analysis must be initiated on the day of receipt and completed within one day of receipt.\*

*\*Note: Samples **known to be high concentration** may be extruded, weighed, and methanol preserved at this point instead of immediately analyzed. Methanol preservation must take place within 1 day of receipt. Once methanol preserved, extracts may be held up to 14 days prior to analysis.*

2.1.2 Option 1b - Collection and Transportation in Coring Devices with Airtight Storage Chambers: Receipt at Laboratory Within 2 Calendar Days of Sampling; Freezing (as Preservation Technique) on Day of Receipt:

Preliminary studies indicate that freezing at  $-12 \pm 3\text{EC}$  (standard food freezer temperature) stops or significantly reduces microbiological degradation and volatilization of VOCs in soil samples.<sup>6</sup> This approach may allow increased pre-analysis holding times without the complications introduced by chemical preservatives. Please see Attachment 2 to this Method, “ISSUE PAPER:

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<sup>5</sup>4EC is the temperature of ice water (water at its highest density). An approximate temperature of 4EC is obtained in the field by placing samples in a cooler filled with ice. 4EC is obtained in the lab through the use of a controlled refrigerator or cold room. The traditional “ $4 \pm 2\text{EC}$ ” is not being specified for IN 5035-M because the intention is not to control the temperatures at 4EC; the intention is to minimize VOC volatilization and microbiological degradation. Temperatures lower than 4EC actually provide superior preservation as compared to maintaining a temperature of  $4 \pm 2\text{EC}$  (see Attachment 2). Lower temperatures are acceptable (even preferable) but will require additional means to obtain and maintain in the field. However, cooler and refrigerator temperatures should not be allowed to exceed 6EC.

<sup>6</sup>David Turriff and Chris Reitmeyer, *Validation of Holding Times for the En Core™ Sampler* (Green Bay, WI: En Novative Technologies, August 1998); U.S. Army Cold Regions Research and Engineering Laboratory, *Storage and Preservation of Soil Samples for Volatile Organic Compound Analysis*, 2<sup>nd</sup> draft unedited, CRREL Special Report by Alan D. Hewitt (Hanover, NH: USACE CRREL, January 1999).

Freezing at  $-12 \pm 3^{\circ}\text{C}$  as a Preservation Technique” for a more detailed discussion.<sup>7</sup>

Multiple collocated aliquots (collocated samples in multiple coring/storage devices) are collected from each sampling location and depth, sealed, and stored on ice in a cooler. The cooler is kept chilled at approximately  $4^{\circ}\text{C}$  and shipped with plenty of ice to the laboratory for receipt within 2 calendar days of sampling

Upon receipt at the laboratory, the chain-of-custody is checked and signed, the samples are logged in, and the samples are frozen at  $-12 \pm 3^{\circ}\text{C}$ . Freezing should take place as soon as possible after arrival at the lab. Samples **must** be placed in the freezer on the day of receipt.\*

The samples may be stored, frozen, for **5** additional calendar days, up to 7 days from the date of collection. As a PBMS approach, longer holding times at  $-12 \pm 3^{\circ}\text{C}$  may be implemented if it can be conclusively demonstrated that the concentrations of target analytes in the samples will not be affected. Determination of whether extended freezer storage is appropriate must be assessed on a project-specific basis, taking into consideration factors such as soil type and specific analytes of concern.

On the date of analysis the unopened coring/storage device is brought to ambient temperature, extruded into a tared vial, and weighed. Reagent water (for low concentration samples) or methanol (for high concentration samples) is added to the unopened vial through the septum, the samples are further prepped as appropriate, and analyzed.

*\*Note: Samples **known to be high concentration** may be extruded, weighed, and methanol preserved at this point instead of frozen. Methanol preservation must take place within 1 day of receipt. Once methanol preserved, extracts may be held at  $4^{\circ}\text{C}$  up to 14 days prior to analysis.*

## **2.2 Option 2: Use of Empty VOA Vials for Sample Transportation and Storage**

This option makes use of pre-tared VOA vials that do not contain chemical preservatives or water-miscible solvents. Sample plugs of appropriate mass are placed into VOA vials in the field and capped, forming an airtight seal. The samples are chilled to approximately  $4^{\circ}\text{C}$  and transported to the laboratory in the hermetically sealed vials.

### **2.2.1 Option 2a - Transfer from Coring Device in Field and Storage to Empty VOA Vial: Receipt at Laboratory Within 2 Calendar Days of Sampling; Analysis Within 1 Additional Calendar Day.**

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<sup>7</sup>IDEM, Office of Solid and Hazardous Waste Management, Technical Waste Assessment Section, “Issue Paper: Freezing at  $-12 \pm 3^{\circ}\text{C}$  as a Preservation Technique,” Attachment 2 to IN 5035-M, (Indianapolis: IDEM, July 1999).

Labeled VOA vials with PTFE-lined septum caps are taken to the field after being tared at the fixed laboratory that will perform the analysis. A small coring device is used to collect multiple collocated aliquots (collocated sample plugs of appropriate mass) from each sampling location and depth. Each sample plug is immediately transferred to the tared vial, which is hermetically sealed (capped) and placed on ice in a cooler. The cooler is kept chilled at approximately 4EC and shipped with plenty of ice to the laboratory for receipt within 2 calendar days of sampling

The laboratory processes samples as soon as possible on the day of receipt. The chain-of-custody form is checked and signed, the samples are logged in, and the capped vial is reweighed to obtain the weight of the sample. The samples are then prepped and analyzed with the caps in place. The vial caps are not removed throughout the entire log-in, storage, preparation and analysis process. All solvents, reference standards, or extract aliquots are introduced or removed via the septum, either manually or mechanically with an automated purge-and-trap system. Analysis must be completed initiated on the day of receipt and completed within one day of receipt.\*

*\*Note: Samples **known to be high concentration** may be weighed and methanol preserved at this point instead of immediately analyzed. Methanol preservation must take place within 1 day of receipt. Once methanol preserved, extracts may be held at 4EC up to 14 days prior to analysis.*

#### 2.2.2 Option 2b - Transfer from Coring Device in Field, Transportation and Storage in Empty VOA Vial: Receipt at Laboratory Within 2 Calendar Days of Sampling; Freezing (as Preservation Technique) on Day of Receipt:

Pre-tared, labeled VOA vials with PTFE-lined septum caps are taken to the field as in Option 2a, above. Multiple collocated aliquots are collected from each sampling location and depth and immediately transferred to the tared vials. The vials are hermetically sealed (capped), chilled to approximately 4EC in a cooler, and shipped with plenty of ice to the laboratory for receipt within 2 calendar days of sampling.

Upon arrival at the lab, the samples are processed as soon as possible on the day of receipt. The chain-of-custody form is checked and signed, the samples are logged in, and the capped vial is reweighed to obtain the weight of the sample. The vials are then frozen at  $-12 \pm 3\text{EC}$ . Freezing should take place as soon as possible after arrival at the lab. Samples **must** be placed in the freezer on the day of receipt.\*

The samples may be stored, frozen, for **5** additional calendar days, up to 7 days from the time of collection. As a PBMS approach, longer holding times at  $-12 \pm 3\text{EC}$  may be implemented if it can be conclusively demonstrated that the concentrations of target analytes in the samples will not be affected.

Determination of whether extended freezer storage is appropriate must be assessed on a project-specific basis, taking into consideration factors such as soil type and specific analytes of concern.

Prior to analysis the sample is brought to ambient temperature then screened, prepped, and analyzed as described in Option 2a above. The vial caps are not removed throughout the entire log-in, storage, preparation and analysis process. All solvents, solutions, or extract aliquots are introduced or removed via the septum, either manually using a syringe with a small gauge needle or mechanically with an automated purge-and-trap system.

*\*Note: Samples **known to be high concentration** may be weighed and methanol preserved at this point instead of frozen. Methanol preservation must take place within 1 day of receipt. Once methanol preserved, extracts may be held at 4EC up to 14 days prior to analysis.*

### **2.3 Option 3: Use of Alternate Procedures Appropriate to Project Objectives: Performance Based Measurement System (PBMS) Approach**

This option allows use of alternate procedures for sampling and analysis appropriate to the site-specific and project-specific Data Quality Objectives (DQOs). The PBMS approach requires provision of a conclusive demonstration that data quality is not compromised by the modifications or substitutions. A conclusive demonstration requires thorough documentation. To ensure appropriateness and adequate data quality, the use of a specific PBMS strategy requires pre-approval by IDEM. If a facility or laboratory does not obtain prior approval and the PBMS approach is found to be inadequate upon submittal of the data to IDEM, resampling and reanalysis will be required.

Guidance for using and documenting a PBMS approach is provided in Appendix IV of the IDEM Non Rule Policy Document, *Guidance to the Performance and Presentation of Analytical Chemistry Data*, (July 1998).<sup>8</sup> A PBMS approach may range from a simple modification to this procedure to the use of entirely different sampling, preparation, or analytical techniques.

## **3.0 INTERFERENCES**

### **3.1 Interferences Leading to False Positives or Biased High Results**

- 3.1.1 Analytical System: Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free

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<sup>8</sup>IDEM, Office of Solid and Hazardous Waste Management, Technical Waste Assessment Section, *Guidance to the Performance and Presentation of Analytical Chemistry Data*, Appendix IV (Indianapolis: IDEM, July 1998), pp. 234-242. (This document is available on the IDEM website at [http://www.state.in.us/idem/oshwm/docs/Guidance/Guidance\\_to\\_Perform\\_Persenta\\_of\\_Analytl\\_Chem\\_Data.pdf](http://www.state.in.us/idem/oshwm/docs/Guidance/Guidance_to_Perform_Persenta_of_Analytl_Chem_Data.pdf))

from contamination under the conditions of the analysis by running method blanks. The use of plastic, non-polytetrafluoroethylene (non-PTFE) coatings and thread sealants or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

- 3.1.2 Diffusion Through Septum: Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.
- 3.1.3 Carryover from High Concentration Samples: Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. Where practical, samples with unusually high concentrations of analytes should be followed by an analysis of organic-free reagent water to check for cross-contamination. If the target compounds present in an unusually concentrated sample are also found to be present in the subsequent samples, the analyst must demonstrate that the compounds are not due to carryover. Conversely, if those target compounds are not present in the subsequent sample, then the analysis of organic-free reagent water is not necessary.
- 3.1.4 Laboratory Solvents: The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken to prevent contamination of samples by methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

### 3.2 Interferences Leading to False Negatives or Biased Low Results

In most materials, VOCs coexist as gaseous, liquid, and solid (sorbed) phases. The VOC equilibrium that exists among these phases is controlled by physicochemical properties, material properties, and environmental variables. Unaccounted loss of analytes from any phase may result in rendering the sample unrepresentative of the material from which it was taken. For this reason, sample collection, handling, and analysis must be performed under conditions that maintain the accountability of all phases present.<sup>9</sup>

3.2.1 Volatilization, Biodegradation, Adsorption and Permeation: Uncontrolled losses of VOCs from materials occur most often through volatilization and biodegradation.<sup>10</sup> In addition some materials (such as PTFE) used in sample storage devices can adsorb VOC molecules or be permeated by VOCs, rendering them unavailable for measurement.

3.2.1.1 *Volatilization* losses occur whenever gaseous phase molecules, which have diffusion coefficients up to four orders of magnitude greater than liquid diffusion coefficients, are allowed to move freely. Therefore, whenever a new surface is exposed, VOC losses are incurred. The extent to which VOCs are lost depends on the vapor phase concentration (analyte vapor pressure), surface area exposed, duration of exposure, and porosity of matrix.<sup>11</sup>

In addition, temperature influences the number of molecules that are in the gaseous phase: increasing temperature increases analyte vapor pressure and decreasing temperature decreases analyte vapor pressure. Therefore, keeping samples iced, refrigerated, or frozen can retard losses to volatilization.

3.2.1.2 *Biodegradation* of VOCs in samples is usually dominated by aerobic processes because many sample collection methods expose the sample to the atmosphere. The rate of biological degradation is dependent on several factors, including the indigenous microbial population, chemical properties of the particular VOC analyte, and temperature. Provided that sufficient quantities of electron acceptors, nutrients, and moisture are present, indigenous microbes continue to aerobically degrade compounds even when stored at 4EC. Aromatic compounds are especially susceptible to this loss mechanism. Freezing samples at  $-12 \pm 3$ EC is effective at stopping microbial activity. Immersion in methanol is also effective.<sup>12</sup>

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<sup>9</sup>ASTM D4547-98, Appendix X1, par. X1.2, p. 8 (direct quote; emphasis added).

<sup>10</sup>Ibid., par. X1.3, p.8.

<sup>11</sup>Ibid.

<sup>12</sup>Ibid., par. X1.4, p. 8.

3.2.1.3 *Adsorption and Permeation:* Teflon and other polymeric materials can adsorb VOCs to some extent and also allow slow permeation of VOC molecules. VOA vials have a Teflon sheet attached to a silicone septum in order to provide a compressible surface that can form an air tight seal against the glass rim. Other sample storage devices use Viton O-Rings against rigid plastic to form the air tight seal. Therefore, extended sample storage periods can lead to analyte loss.<sup>13</sup>

3.2.1.4 *Minimizing Losses from Volatilization, Biodegradation, and Adsorption.*<sup>14</sup>

- A. Collect samples only from freshly exposed soil or waste surfaces;
- B. Collection and transfer of samples should be performed quickly and with minimal disruption to its physical state;
- C. If possible, the number of transfer steps between collection of sample and placement in final vial should be limited to 1, and subsampling should be avoided;
- D. If possible, samples should not be held more than 48 hours at approximately 4EC; longer storage periods should be at  $-12 \pm 3\text{EC}$ ;
- E. Samples should only be stored in hermetically sealed chambers (such as VOA vials or the En Core™ Sampler); and
- F. The VOA vial's airtight seal should never be broken prior to analysis (whether sealed in the field after collection, in the lab after extrusion from an En Core™ Sampler, or in the lab after dilution of an aliquot of high level sample extract).

3.2.1.5 *Methanol peak interference in high level sample extracts:* When high concentration samples are extracted with methanol, it is possible that the resulting methanol peak in the chromatogram could interfere with the peaks of the VOCs of interest.<sup>15</sup> Whether this creates a problem will depend on the retention times of methanol and of the target VOCs on the chromatographic column used.

3.2.1.6 *Incomplete extraction or desorption from the sample matrix* can result in underestimated results.<sup>16</sup> The sampled material should be well dispersed in the methanol or reagent water. Sonication or other agitation is recommended prior to and during the purge-and-trap process.

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<sup>13</sup>Hewitt, p. 18.

<sup>14</sup>ASTM D 4547-98, par. X1.6, p. 8.

<sup>15</sup>ASTM D 4547-98, par. 6.2.2, p. 2.

<sup>16</sup>Ibid., Appendix X1, par. X1.7, p. 9.

## 4.0 APPARATUS AND MATERIALS

### 4.1 Sample Containers

The specific sample containers required will depend on the purge-and-trap system to be employed (see Sec. 4.2). Several systems are commercially available. Some systems employ 40-mL clear vials with a special frit and equipped with two PTFE-faced silicone septa. Other systems permit the use of any good quality glass vial that is large enough to contain at least 5 g of soil or solid material and at least 10 mL of water and that can be sealed with a screw-cap containing a PTFE-faced silicone septum. Consult the purge-and-trap system manufacturer's instructions regarding the suitable specific vials, septa, caps, and mechanical agitation devices.

### 4.2 Purge-and-Trap System

The purge-and-trap system consists of a unit that purges the VOCs using an inert gas stream while agitating the contents of the vial, and also traps the released VOCs for subsequent desorption into the gas chromatograph. Some systems also are able to automatically add water, surrogates, and internal standards to a vial containing the sample. The purge-and-trap system used should meet the following specifications. (See SW-846 Method 5035 (December 1996 Section 4.2 for a more detailed description.)

4.2.1 Purging Chamber: The purging device should be capable of accepting a vial sufficiently large to contain a 5-g soil sample plus 10 mL of water. The device must be capable of heating a soil vial to 40EC and holding it at that temperature while the inert purge gas passes through the sample. It should also be capable of agitating the sealed sample during purging, using sonication or other means. The analytes being purged must be quantitatively transferred to an absorber trap. The trap must be capable of transferring the absorbed VOCs to the gas chromatograph.

For ease of sample preparation, the lab may use a device that is capable of automatically introducing at least 5 mL of organic-free reagent water into the sample vial while trapping the displaced headspace vapors.

4.2.2 Traps and Trapping Materials: A variety of traps and trapping materials may be used with this method. The choice of trapping material may depend on the analytes of interest. Whatever trap is used must demonstrate adequate adsorption and desorption characteristics to meet the quantitation limits of all target analytes required for a given project. It must also meet the QC requirements in the project-specific Quality Assurance Project Plan (QAPP) and in the determinative method. The trap must be capable of absorbing the early eluting gases and of desorbing the late eluting target analytes. Examples of appropriate traps and trapping material combinations include:

- 4.2.2.1 *Trap used to develop SW-846 Method 5035 (December 1996):* A 25-cm long trap with an inside diameter of 0.105 inches, packed with Carbopack/Carbosieve (Supelco, Inc.).
- 4.2.2.2 *Standard trap used in EPA purge-and-trap methods:* A 25-cm long trap with an inside diameter of 0.105 inches, packed with equal amounts of the adsorbents listed in A. through C. below, starting from the inlet. It is recommended that 1.0 cm of methyl silicone-coated packing (35/60 mesh, Davison, grade 15 or equivalent) be inserted at the inlet to extend the life of the trap.
- A. 1/3 total length of 2,6-diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenzx GC or equivalent);
  - B. 1/3 total length of methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh (or equivalent), and
  - C. 1/3 length of coconut charcoal - prepared from Barnebey Cheney CA-580-26 (or equivalent) by crushing through a 26 mesh screen.
- 4.2.3 Desorber: The desorber for the trap must be capable of rapidly heating the trap to the temperature recommended by the trap material manufacturer, prior to the beginning of the flow of desorption gas.

#### **4.3 Syringes and Syringe Valves**

- 4.3.1 Hypodermic Syringe for : 25-mL glass hypodermic syringes with Luer-Lok (or equivalent) tip (other sizes are acceptable depending on sample volume used).
- 4.3.2 Syringe Valves: 2-way syringe valves with Luer ends.
- 4.3.3 Micro Syringe for : 25- $\mu$ L micro syringe with a 2 inch x 0.006 inch ID, 22E bevel needle (Hamilton #702N or equivalent).
- 4.3.4 Micro Syringes for: 10-FL, 100- $\mu$ L.
- 4.3.5 Syringes for: 0.5-mL, 1.0-mL, and 5-mL, gas-tight with shut-off valve.

#### **4.4 Miscellaneous Apparatus and Equipment**

- 4.4.1 Glass Vials: 40-mL (or size appropriate to fit analyzing laboratory's autosampler) with PTFE-lined, septum-sealed screw-cap. Examine each vial prior to use to ensure that the vial has a flat, uniform sealing surface.

Note (1): If desired, aliquots for dry weight determination may be collected in septum-sealed, 60-mL glass vials or PTFE-lined 2-ounce or 4-ounce VOA jars.

Note (2): Project DQOs or site conditions may require the collection of larger sample volumes to ensure adequate sample mass. Size of sample containers may need to be adjusted accordingly:

**S** When *analytical considerations* require collection of larger size sample plugs (e.g., 25 grams) 60 mL VOA vials may be required.

**S** Certain *soil matrices* (such as very wet soil, material with very high organic content, or material with large particle size) might involve collection of samples that cannot form cohesive plugs and require larger sample jars with PTFE-lined lids.

4.4.2 Top-Loading Balance: Capable of accurately weighing to 0.01 g.

4.4.3 Glass Scintillation Vials (for dilution of oily waste samples): 20-mL, with screw-caps and PTFE liners, or glass culture tubes with screw-caps and PTFE liners.

4.4.4 Volumetric Flasks: Class A, 10-mL and 100-mL, with ground-glass stoppers.

4.4.5 2-mL Glass Vials (for oily waste samples extracted with methanol or PEG) for introduction of diluted waste samples using GC autosampler.

4.4.6 Stainless Steel Spatula: to be used for screening, dry weight, and oily waste aliquots (or, **if absolutely necessary**, for high concentration samples). The spatula should narrow enough to fit into a sample vial.

4.4.7 Disposable Pasteur pipettes.

4.4.8 Small ziplock bags: Sandwich or snack size, foil or plastic, for storage and transportation of tared sample vials.

## 4.5 Field Sampling Equipment

4.5.1 Coring Devices for Sampling Materials that Will Form Cohesive Plugs (including tight clays):

Please see the “Sampling Equipment Issue Paper” for more complete descriptions with illustrations and diagrams.<sup>17</sup>

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<sup>17</sup>IDEM, Office of Solid and Hazardous Waste Management, Technical Waste Assessment Section, “Sampling Equipment Issue Paper,” (Indianapolis: IDEM, June 1999).

4.5.1.1: *En Core™ Sampler*:<sup>18</sup> (En Novative Technologies, Inc., 1241 Bellevue Street, Green Bay, WI 54302; Phone: (888) 411-0757; Fax: (920) 465-3963; e-mail: [info@ennovativetech.com](mailto:info@ennovativetech.com)), or equivalent. This device may be used for collection and transportation to the laboratory as described in **Option 1**.

4.5.1.2: *EasyDraw Syringe™* and *Powerstop Handle™*:<sup>17</sup> (U.S. Oil Company, Inc., Analytical Laboratory Services, 1090 Kennedy Avenue, Kimberley, WI 54136; Phone: (800) 490-4902; Fax: (920) 739-1738; e-mail: [laboratory@usoil.com](mailto:laboratory@usoil.com)), or equivalent. This device may be used as a coring device for collection prior to transfer to VOA vials as described in **Option 2**.

4.5.1.3: *Purge-and-Trap Soil Sampler - Model 3780PT*:<sup>17</sup> (Associated Design and Manufacturing Company, 814 North Henry Street, Alexandria, VA 22314; Phone: (800) 837-8257; Fax: (703) 548-0919), or equivalent. This device may be used as a coring device for collection prior to transfer to VOA vials as described in **Option 2**.

4.5.1.4 *Modified Syringe*: Disposable plastic syringes with a barrel smaller in diameter than the neck of the soil vial may be modified for use as a coring device by cutting off the syringe end of the barrel prior to sampling. Modified syringes may be used for collection of 5-gram soil aliquots under **Option 2**.

#### 4.5.2 Sampling Equipment for Use When Coring Devices Are Not Suitable for Soil or Waste Characteristics

4.5.2.1 *Chisel (for rock and other cemented material)*: A chisel is used to fragment large pieces of hard or cementitious material to a size that can be put in a VOA vial.

4.5.2.2 *Scoop or Spatula (for noncohesive materials such as dry sand, gravel, peat, and very wet soils)*: Scoops or spatulas are used to transfer material that will not form a cohesive plug into a sample container or sample storage device. Choice of scoop or spatula will depend on grain size of material to be sampled and size of sample container.

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<sup>18</sup>The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an endorsement or exclusive recommendation for use by IDEM. The products cited in IN 5035-M represent those products: (a) of which IDEM had knowledge at the time the method was written and (b) for which IDEM had confidence based on review of studies performed using that equipment, EPA approval, or both. Equipment other than that listed may be used provided that the resulting method performance meets the project data quality objectives and has been documented as described in SW-846 Chapter Two, Section 2.1.

## 5.0 REAGENTS

- 5.1 Organic-free reagent water:** All references to water in this method refer to organic-free reagent water, as defined in Chapter One.
- 5.2 Methanol, CH<sub>3</sub>OH:** purge-and-trap quality or equivalent. Store away from other solvents.
- 5.3 Polyethylene glycol (PEG), H(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OH :** free of interferences at the detection limit of the target analytes.
- 5.4 Internal standards, surrogate standards, and spiking compounds:** See the determinative GC or GC/MS method and SW-846 Methods 5000 and 8000 for guidance on choosing compounds employed in this procedure.

## 6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Refer to Sections 2.1 through 2.4, for general sample collection information for the available options. Refer to Section 4.1 for general information regarding sample vials. The actual sample vials used must be appropriate for any autosamplers that will be used at the analyzing laboratory. Refer to Sections 4.5.1 through 4.5.3 for descriptions and general instructions regarding the use of field sampling equipment appropriate to the available collection options and material to be sampled.

**Note (1):** The collection of bulk samples (e.g., in large bottles or traditional wide-mouth 4-oz. VOA jars) that would require laboratory subsampling is not an option under IN 5035-M except as a PBMS approach when pre-approved by IDEM, or when certain specialized materials must be sampled. (See Section 6.1.4.) In addition, IDEM will not approve PBMS proposals for collection of bulk soil samples unless samples are known to contain high VOC concentrations (exceeding the linear range of low level calibration curve) and benzene is not a contaminant of concern.

**Note (2):** Preservation/extraction of samples with methanol is not appropriate for low concentration samples analyzed by the closed-system purge-and-trap method described in IN 5035-M except as a PBMS approach when pre-approved by IDEM. Samplers and analysts should be aware of three potential problems with the use of methanol:

- (a) ***Quantitation limits:*** The use of methanol as a preservative and extraction solvent introduces a significant dilution factor that will raise the method quantitation limit beyond the operating range of the low concentration direct purge-and-trap procedure. This will make it difficult to demonstrate compliance with regulatory limits or action levels for some analytes.

- (b) ***Ignitability characteristic:*** The addition of methanol to the sample is likely to cause the sample to fail the ignitability characteristic, thereby making the unused sample volume a RCRA hazardous waste.\*

**\*Note:** *Dealing with Laboratory Hazardous Waste:* Per the *Code of Federal Regulations* 40 CFR 261.4(d), analytical samples are excluded from RCRA hazardous waste regulation (even if exhibiting a characteristic) while being:

- Stored in the lab before testing,
- Stored in the lab after testing for a specific purpose,
- Stored in the lab after testing before being returned to the sample collector, and
- Transported back to the sample collector.

If methanol-containing samples that fail the ignitability test will not be returned to sample collector, they will have to be stored away from ignition sources until disposal can be arranged. For guidance in on-site handling, lab packing, and off-site disposal, see a waste management handbook, such as: ACS Task Force on Laboratory Waste Management, *Laboratory Waste Management: A Guidebook*, Washington, D.C.: American Chemical Society, 1994.

- (c) ***Sample moisture content:*** Any free water present in the sample will be miscible with the methanol and extracted along with the volatile analytes. This will volumetrically increase the extract phase, resulting in a dilution of the analytes extracted from the sample *and* a dilution of the surrogates, internal standards, and matrix spikes. Calculations should be adjusted to account for this dilution (see below).

**If methanol must be used, (a) in the field because of physical characteristics of the matrix (e.g., rocks or cemented materials) or (b) in the lab to extract high concentration samples, samples must be introduced to the instrument using SW-846 Method 5030 purge-and-trap (or equivalent) or SW-846 Method 5021 equilibrium headspace analysis (or equivalent). Calculations should also be adjusted based on sample moisture content:**

The moisture content of the sample can be determined from the dry weight determination. Once the moisture content is known, results can be corrected by multiplying the “observed concentrations” (based on the volume of methanol alone) by the ratio: 
$$\frac{\text{volume of methanol} + \text{water}}{\text{volume of methanol}}$$

## 6.1 Preparation of sample containers

Sample containers should be prepared in a fixed laboratory or other controlled environment, sealed, and shipped to the field location. The specific preparation procedures for sample containers prior to sampling depends on the collection and storage option selected in conjunction with the physical characteristics of the soil or waste to be sampled. If vials will be used in the field (i.e., if Option 2 is selected or samples will include rock or gravel), it is recommended that vial preparation is done in the same laboratory that will analyze the samples. This will ensure that the vials provided will

work in the purge-and-trap system that will be used. Gloves should be worn while handling and taring vials.

After sampling is completed, the filled containers are returned to the analytical laboratory. Further sample preparation steps depend on the expected concentration range of the sample, with separate preparation procedures for low concentration soil samples, high concentration soil, and oily waste samples. Gloves should be worn during the preparation steps.

6.1.1 Option 1: Use of Coring Devices with Airtight Storage Chambers for Sampling and Transportation: The disposable EnCore™ Sampler (or equivalent) functions as both sampling tool and air tight sample container for transportation to the laboratory. The En Core™ Sampler comes in two sizes. Each contains a single storage chamber with a volume corresponding to either approximately 5 grams or approximately 25 grams soil mass based on average soil density.

6.1.1.1 *Aliquots for screening and determinative analysis:* Each 5-gram sampler with end cap is individually packaged in a sealed, labeled foil ziplock bag with usage instructions attached. No pre-sampling container preparation is required, other than entering preliminary sample identification information on the label.

Note: Certain site conditions may require the collection of the determinative aliquots in 25-gram size samplers to ensure adequate sample mass. Examples might include very wet soil, such as soil sampled from wetland areas, or material with very high organic content, such as peat.

6.1.1.2 *Dry weight aliquot:* For remediation projects (and for all samples that will be extracted with methanol), a dry weight aliquot must be collected from each sampling location. At least 5 to 10 grams of soil are necessary for the analysis. The dry weight aliquot may be collected in a 25-gram size EnCore™ Sampler (or equivalent). Alternatively, it may be collected in a glass container such as a VOA vial or 4-oz. jar using a scoop or spatula. Label the type of container called for in the sampling plan. Include the words “dry weight” in the sample description. It is not necessary to tare the container for the dry weight aliquot.

6.1.2 Option 2: Use of Empty VOA Vials for Sample Transportation and Storage: The vials used must have PTFE-lined septum caps and must be appropriate for the purge-and-trap system that will be utilized for analysis. Preparation steps:

6.1.2.1 Seal the vial with the screw-cap and septum seal. If the double-ended, fritted, vials are used, seal both ends as recommended by the manufacturer.

- 6.1.2.2 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).
- 6.1.2.3 Weigh the labeled vial to the nearest 0.01 g, record the tare weight, and write it on the label.
- 6.1.2.4 Insert the tared vial into an individual ziplock bag and seal. The ziplock bag should be labeled. The same information written on the vial label should be included on the bag label.
- 6.1.2.5 Because volatile organics will partition into the headspace of the vial from the sample and will be lost if the vial is opened, surrogates, matrix spikes, and internal standards should only be added to the vials after the sample has been added to the vial and the vial has been sealed. These standards should be introduced in the laboratory, through the septum of the sealed vial just prior to analysis, either manually using a small-gauge needle or automatically by the sample introduction system.
- 6.1.2.6 *Dry weight aliquot:* For remediation projects (and for all samples that will be extracted with methanol), a dry weight aliquot must be collected from each sampling location. At least 5 to 10 grams of soil are necessary for the analysis. The dry weight aliquot may be collected similarly to the aliquots that will be used for screening and determinative analysis (with a coring device), except that a minimum of 2 cores (or one larger core) should be collected to ensure adequate sample mass. Alternatively, the dry weight aliquot may be collected in the traditional manner, using a scoop or spatula to fill a VOA vial or 4-oz. jar. Label the type of container called for in the sampling plan. Include the words “dry weight” in the sample description. It is not necessary to tare the container for the dry weight aliquot.
- 6.1.3 When Material to be Sampled is Rock, Other Cemented Material, or Gravel: Use of VOA vials Containing Methanol: **Samples collected using this variation must be purged by SW-846 Method 5030 or introduced by an equilibrium headspace technique such as SW-846 Method 5021 (or equivalent).**
  - 6.1.3.1 Add 5 mL of methanol to each vial.
  - 6.1.3.2 Seal the vial with the screw-cap and septum seal.
  - 6.1.3.3 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

6.1.3.4 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label. **When possible, the vial with methanol should be tared on the same day it is to be used.**

6.1.3.5 Insert the tared vial into an individual ziplock bag and seal. The ziplock bag should be labeled. The same information written on the vial label should be included on the bag label.

6.1.3.6 Surrogates, internal standards, and matrix spikes (if applicable) should be added to the sample vial after it is returned to the laboratory and prior to analysis.

6.1.3.7 *Dry weight aliquot:* For each sampling location, label one additional sample container. Include the words “dry weight” in the sample description. **Do not add methanol to this container.** The vial for the dry weight aliquot does not need to be tared.

6.1.4 When Material to be Sampled is Very Wet Soil (as in a Wetland Area), Sediment from Surface Water Bodies, Organic Material Such as Mulch or Peat:

Soils, sediments, and fills with very high moisture or organic content or materials with large or heterogeneous particle size are unlikely to form cohesive plugs. Also, the lower density or large particle size of these materials may not allow sample mass sufficient for analysis to be collected in VOA vials.

Based on knowledge of the material to be sampled, select and label glass containers of sufficient size with PTFE-lined lids. 8-ounce to 32-ounce jars may be required. Laboratory subsampling is unavoidable for these materials, so taring of containers is not required.

6.1.5 Preparation of Containers for Oily Waste Samples :

Oily waste samples will be diluted in the laboratory with an appropriate solvent and analyzed as a high concentration sample. If the waste is soluble in methanol or other water-miscible solvents, it will be introduced using SW-846 Method 5030 or SW-846 Method 5021 (or equivalent). If the waste is not soluble in methanol, it will be diluted with another solvent such as *n*-hexadecane using SW-846 Method 3585.

Because oily wastes will be subsampled and diluted in the lab, it is not necessary for the vials to be suited to the lab's autosampler. Also, the vials do not need to be tared. Two labeled, septum-seal vials should be collected per sampling location. This should allow sufficient sample volume for solubility testing, screening, definitive analysis and MS/MSD analysis (when appropriate). Dry weight is generally not determined for oily wastes.

## 6.2 Sample Collection

Collect the sample according to the procedures outlined in the sampling plan. The project-specific sampling plan should incorporate the appropriate portions of these instructions to meet site-specific conditions and project DQOs in conjunction with the collection Option chosen. If Option 2 is chosen, VOA vials pre-tared at the laboratory will be taken to the field. Gloves should be worn whenever handling the tared sample vials. As with any sampling procedure for volatiles, care must be taken to minimize the disturbance of the sample in order to minimize the loss of the volatile components.

#### 6.2.1 Sampling of Cohesive Materials

The procedures in this section apply to cohesive but uncemented soils (and solid wastes) that will form a cohesive plug when sampled with a small coring device. This should include the majority of soil types (and some solid waste types) that will be sampled for volatile organic analysis.

##### 6.2.1.1 **Option 1: Use of Coring Devices with Airtight Sample Chambers**

The following sample collection instructions apply to both Option 1a (Analysis Within 1 Day of Receipt at the Laboratory) and Option 1b (Freezing within 1 Day of Receipt at the Laboratory):

- A. *Description of Process:* The En Core™ Sampler (or equivalent) is designed to collect, transport, and deliver intact soil sample plugs. The coring body of the sampler is pushed into a freshly exposed soil surface, obtaining a headspace-free plug. The sample chamber is then sealed with the cap, becoming airtight. Once back at the laboratory, the sample plug is extruded into a tared VOA vial and frozen for storage or prepped for immediate analysis.
- B. *Multiple Collocated Aliquots:* To allow for concentration range screening, determinative analysis, and reanalysis (when necessary), a minimum of three collocated aliquots (3 filled 5-gram En Core™ Samplers, or equivalent) are collected from each sampling location and depth, capped, and stored at 4EC.
  - i.) MS/MSD: An additional 2 collocated aliquots should be collected for samples chosen to be spiked as matrix spike/matrix spike duplicates. That is, 5 collocated En Core™ Samplers (or equivalent) should be collected to include the MS/MSD.
  - ii.) Dry weight aliquot: For remediation projects (and for all samples that will be extracted with methanol), a dry weight aliquot must be collected from each sampling location. A minimum of 5 to 10 grams mass is required. To ensure sufficient mass is collected, the aliquot to be used for dry weight analysis should be collected in either a 25-gram En

Core™ Sampler (or equivalent), or in a traditional VOA vial or 4-ounce jar (using a spatula or scoop).

C. *En Core™ Sampler (or equivalent) Sampling Steps:*<sup>19</sup>

- i.) Remove the sampler and cap from foil the package and attach the reusable T-handle to the sampler body.
- ii.) Quickly push the sampler into a freshly exposed surface of soil until the sampler is full.
- iii.) Use paper toweling to quickly wipe the sampler head so that the cap can be tightly attached.
- iv.) Push the cap on with a twisting motion to firmly attach.
- v.) Detach the T-handle from the capped sampler.
- vi.) Fill out the label and attach to sampler.
- vii.) Repeat the procedure for the other 3 (to 5) samplers.
- viii.) If dry weight sample is being collected in a glass vial or jar, collect using a spatula; fill the container.

Immediately upon capping, each filled En Core™ Sampler (or equivalent) is placed back into its zip-lock foil bag and placed on ice in a cooler. The cooler is kept chilled at approximately 4EC and shipped with plenty of ice to the laboratory for receipt within 2 calendar days of sampling.

6.2.1.2 **Option 2: Use of Empty (Non-Preserved) VOA Vials for Sample Transportation and Storage**

The following sample collection instructions apply to both Option 2a (Analysis Within 2 Calendar Days of Sampling) and Option 2b (Freezing within 2 Days of Sampling):

Several techniques are available to transfer a sample plug of about 5 grams to the relatively narrow opening of the VOA vial. These include using coring devices such as the EasyDraw Syringe™ and Powerstop Handle™, the Purge-and-Trap Soil Sampler™, and a cut plastic syringe. Any equivalent device may also be used.<sup>20</sup>

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<sup>19</sup>En Novative Technologies, Inc., SW 846 Method 5035 Field Sampling Guide, "En Core™ Sampler Collection for Low Level Analyses (\$1 Fg/kg)," (Green Bay, WI: En Novative Technologies, 1998), photocopy.

<sup>20</sup>The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an endorsement or exclusive recommendation for use by IDEM. The products cited in IN 5035-M represent those products: (a) of which IDEM had knowledge at the time the method was written and (b) for which IDEM had confidence based on review of studies performed using that equipment, EPA approval, or both. Equipment other than that listed may be used provided that the resulting method performance meets the project data quality objectives and has been documented as described in SW-846 Chapter Two, Section 2.1.

- A. *Description of Process:* A small coring device is used to obtain a surface sample or to obtain a subsurface sample from a boring. The sample plug is immediately transferred to the tared vial and hermetically sealed (capped). Collection of the next collocated plug does not begin until the previous plug is hermetically sealed in its vial. Immediately upon capping, each filled vial is placed in a zip-lock bag (foil or plastic) and placed on ice in a cooler. The cooler is kept chilled at approximately 4EC and shipped with plenty of ice to the laboratory for receipt within 2 calendar days of sampling
- B. *Multiple Collocated Aliquots:* To allow for concentration range screening (optional), determinative analysis, and reanalysis (when necessary), a minimum of three collocated aliquots (3 sealed VOA vials containing sample plugs) are collected from each sampling location and depth and stored at 4EC.
- i.) MS/MSD: An additional 2 collocated aliquots should be collected for samples chosen to be spiked as matrix spike/matrix spike duplicates. That is, 5 collocated sample plugs, each hermetically sealed in its own tared vial, should be collected to include the MS/MSD.
- ii.) Dry weight aliquot: For remediation projects (and for all samples that will be extracted with methanol), a dry weight aliquot must be collected from each sampling location. An additional aliquot with a minimum mass of 5 to 10 grams is required. The dry weight aliquot may be collected *either* in the traditional way (using a spatula to fill a VOA vial or 4-ounce VOA jar) or using a coring device and transferring the sample plugs to a vial. If a 5-gram coring device is used, it is recommended that 2 to 3 plugs are placed in the dry weight vial to ensure that adequate sample mass is available. The spatula technique may not be used for aliquots that will be used for screening or determinative analysis.
- C. *Sampling Steps:* The exact sampling steps will depend on the coring device selected.
- i.) Use of the EasyDraw Syringe™ and Powerstop Handle™ (or equivalent). The soil plug is obtained with the sampling device and transferred into a VOA vial in the field. The

Powerstop Handle™ is reusable; however, a new syringe must be used for each sampling location.<sup>21</sup>

Sampling Steps: There are three 5-gram positions and three 10-gram positions on the Powerstop Handle™. The three positions are labeled light, medium, and heavy to correspond to low, medium, and high soil densities. There is also one 13-gram position. In general (unless project DQOs or site conditions indicate a larger sample size is required) one of the 5-gram positions will be used to collect all aliquots except those for screening and dry weight. The corresponding 10-gram position or the 13-gram position should be used for the screening and dry weight aliquots.

- (a) Select the appropriate 5-gram slot on the Powerstop Handle™ to ensure collection of correct soil mass. As a general guide, refer to Table 2, "Some Typical Values for Different Densities of Some common Soil Materials" (p. 52). Alternatively, use the following guidelines:
  - (1) Use the heavy position for dense clay;
  - (2) Use the light position for dry sandy soil and soil with high organic content (except dry peat. If dry peat is sampled, use the 10-gram light position.)
  - (3) Use the medium position for all other soil types.
- (b) Load the sampling device by inserting the EasyDraw Syringe™ into the slot on the Powerstop Handle™ selected in step (a). Remove end cap from syringe.
- (c) Collect sample by pushing the EasyDraw Syringe into a freshly exposed soil surface. Continue pushing until the soil column inside the syringe has forced the plunger to the stopping point.
- (d) Put the end cap back on the syringe to prevent loss of any loose material and remove the syringe from the handle device. Quickly wipe the exterior of the barrel with a clean disposable towel.
- (e) Remove the syringe end cap and insert the syringe into the pre-tared VOA vial. Eject the sample into the vial by pushing on the syringe plunger.
- (f) Wipe any soil off the vial threads with paper toweling and cap the vial, hermetically sealing.

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<sup>21</sup>U.S. Oil, U.S. Analytical Laboratory, "How to Collect Soil Samples with the EASYDRAW SYRINGE™ and the POWERSTOP HANDLE™," file STEPSIII 5035.doc, (U.S. Oil, 1999).

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- (g) Repeat the procedure (refilling the same syringe each time) for the remaining collocated aliquots intended for determinative analysis.
- (h) The dry weight and screening aliquots may be collected the same way, except inserting syringe into a 10-gram slot to collect greater sample volume. The dry weight aliquot does not need to be transferred to a vial; the filled syringe may be capped with the end cap and transported to the laboratory. (Alternatively, the dry weight sample may be collected by using a spatula or scoop to fill a vial or jar.)
- (i) Repeat steps (b) through (h) with a new syringe at each additional sampling location.

Immediately upon capping, each vial with sample plug is placed in a zip-lock bag (plastic or foil) and placed on ice in a cooler. The cooler is kept chilled at approximately 4EC and shipped with plenty of ice to the laboratory for receipt within 2 calendar days of sampling.

- ii.) Use of Purge-and-Trap Soil Sampler™ (or equivalent): The soil plug is obtained with the sampling device and transferred into a VOA vial in the field, sealed, chilled to approximately 4EC, and transported to the laboratory:
  - (a) Follow manufacturer's instructions to obtain the sample plug from a freshly exposed soil surface with the device. Wipe the exterior of the barrel with a clean disposable towel prior to extruding sample to vial.
  - (b) Wear gloves during all handling of pre-weighed vials.
  - (c) Follow manufacturer's instructions to extrude the soil core into the VOA vial.
  - (d) Wipe any soil off the vial threads with paper toweling and cap the vial, hermetically sealing.
  - (e) Repeat procedure for the other 3 (to 5) collocated aliquots.
  - (f) The dry weight aliquot may be collected the same way. Alternatively, the dry weight sample may be collected by using a spatula to fill a vial or jar.

Immediately upon capping, each vial with sample plug is placed in a zip-lock bag and placed on ice in a cooler. The cooler is kept chilled at approximately 4EC and shipped with plenty of ice to the laboratory for receipt within 2 calendar days of sampling.

- iii.) Use of a modified plastic syringe as a coring device

Disposable plastic syringes can be easily converted to inexpensive coring devices. One syringe is needed for each sampling location.

(a.) *Pre-sampling preparation steps: coring device preparation and estimate of soil volume for 5 grams:*  
The following preparations should be performed in a clean environment.

- (1) Have at least 1 disposable 5- or 10-mL syringe per sampling location, plus a few extras. All the syringes used for a specific project should be the same size and type for ease in obtaining appropriate weight samples (through volume measurement).
- (2) Cut off the “needle end” of the syringe barrel, thus creating a blunt, even coring end.
- (3) Remove the rubber cap from the plunger.
- (4) Determine the soil volume that will yield *approximately 5-gram samples*.<sup>22</sup>
  - (A) Using soil similar in type to the soil at the sampling site, collect several trial samples of varying length with the “extra” modified syringes.
  - (B) Weigh each trial sample on a top-loading balance and note the length of the soil column in the syringe.
  - (C) Use these data to determine the length of soil in the syringe that corresponds to approximately 5 grams. This length will be used for all samples collected on site.
  - (D) Discard the syringes used to determine sample length and the trial samples.

(b) *Field Sampling Steps:*

- (1) Collect the sample by pushing the cut end of a modified syringe into a freshly exposed soil (or waste) surface.

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<sup>22</sup>Note: The 5-gram sample size is an *approximate* (not an absolute) requirement, and samples are weighed only to  $\pm 0.01$  grams. Therefore varying density of on-site soil types should be insignificant in most cases. However, if the areas or depths to be sampled are known to contain widely varying soil types (e.g., a peat bog and an area of dense clay or glacial till), it would be advisable to determine volumes for each of the distinct soil types.

- (2) Continue pushing until the soil column inside the syringe has forced the plunger to length determined to yield approximately 5 grams in the pre-sampling preparation phase.
- (3) Quickly wipe the exterior of the barrel with a clean disposable towel.
- (4) Insert syringe into the open end of the pre-tared VOA vial. Extrude sample into the vial by pushing on the syringe plunger.
- (5) Quickly wipe any soil off the vial threads with paper toweling and cap the vial, hermetically sealing.
- (6) Repeat procedure for the other 3 (to 5) collocated aliquots at the sampling location or depth. Discard the syringe after all collocated aliquots are collected for the sampling location.
- (7) The dry weight aliquot may be collected the same way (before discarding the syringe). Alternatively, the dry weight sample may be collected by using a spatula to fill a vial or jar.
- (8) Begin with a fresh, unused syringe at the next sampling location or depth.

Immediately upon capping, each vial with sample plug is placed in a zip-lock bag (plastic or foil) and placed on ice in a cooler. The cooler is kept chilled at approximately 4EC and shipped with plenty of ice to the laboratory for receipt within 2 calendar days of sampling.

#### 6.2.2 Sampling Cemented Soils and Wastes (including rocks):

The procedures in this section apply to hard or cementitious materials that cannot be sampled with a small coring device.

6.2.2.1: *Use of Chisel:* Samples of cemented material may be obtained by fragmenting a larger portion of the material with a clean chisel to generate aggregate(s) of a size that can be placed into a VOA vial.

When transferring the piece(s) of aggregate, care must be taken to prevent compromising the sealing surfaces and threads of the container. Losses of VOCs by using this procedure are dependent on the location of the contaminant relative to the surface of the material being sampled. **Caution should be taken in the interpretation of data from materials collected in this way.**<sup>23</sup>

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<sup>23</sup>ASTM D 4547-98, par. 7.5.1, p. 5. (Emphasis added.)

- 6.2.2.2 **Option 2**, the “empty VOA vial” method, is **not recommended** for pieces of cementitious material unless it can be conclusively shown that the technique does not compromise the concentrations of target analytes in the samples.
- 6.2.2.3 **Option 1** (coring devices with airtight sample chambers) **should not be used for rocks**. Such devices are not effective for rocks and other cementitious materials.<sup>24</sup>
- 6.2.2.4 *Cap vials quickly* after collecting the appropriate weight or volume of sample. Immediately upon capping, place each vial in a zip-lock bag (plastic or foil) and put in a cooler. The cooler is kept chilled at approximately 4EC and shipped with plenty of ice to the laboratory for receipt within 2 calendar days of sampling.

6.2.3 Sampling Fine-Grained, Noncohesive Soils and Wastes (including sand and gravel):

The instructions in this section apply to uncemented soils and solid wastes that will not readily form a cohesive plug. Since a cohesive plug cannot be formed, small coring devices cannot be used as described in Section 6.2.1.

- 6.2.3.1 *Wet sand*: If the material to be sampled will form a cohesive plug, it can be sampled using coring devices as described in section 6.2.1.
- 6.2.3.2 *Dry sand, gravel, gravel/fines mixtures, and other materials (wet or dry) that will not form cohesive plugs* can be sampled by using a scoop or spatula to quickly transfer approximately 5 grams into an empty, tared VOA vial, or into a VOA vial tared with methanol.

Care should be taken not to compromise the vial’s sealing surfaces and threads and, if liquid is present, to avoid loss of solvent from splashing or spilling.<sup>25</sup> The vial should then be immediately hermetically sealed (capped), placed in a zip-lock bag (foil or plastic), and put on ice in a cooler, and shipped to the laboratory as in Options 2 or 3, above.

If dry weight will be determined, the dry weight aliquot must be collected in a container that does not contain methanol.

- 6.2.3.3 *Alternative procedure for wet or dry sand or soil that will not form cohesive plugs*: Coring devices with airtight sample chambers (such

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<sup>24</sup>En Novative Technologies, Inc., Frequently Asked Questions (FAQ), (Green Bay, WI: En Novative Technologies, 1998), photocopy.

<sup>25</sup>ASTM D 4547-98, par. 7.6.1, p. 6.

as the En Core™ Sampler or equivalent) can be used for collection and transportation of fine-grained non-cohesive samples in the following manner:

- A. Pull the plunger back to form an o-ring seal at the back end of the body.
- B. Maintaining the plunger in this position, scoop the sand or soil into the storage chamber with a spatula until it is completely filled.
- C. Attach and seal the cap, creating an airtight, headspace-free condition.<sup>26</sup>
- D. Immediately upon capping, the filled En Core™ Sampler (or equivalent) is placed back into its zip-lock foil bag and placed on ice in a cooler. The cooler is kept chilled at approximately 4EC and shipped with plenty of ice to the laboratory for receipt within 2 calendar days of sampling.
- E. The aliquot for dry weight determination may be collected in the same way, following steps (i - (iv, using a 25-gram size sampler. Alternatively, a glass vial or jar may be used.

**Coring devices with airtight sample chambers should not be used for gravel.**

6.2.4 Sampling Noncohesive or Semicohesive Materials with Very High Moisture Content, Very High Organic Content, or Large or Heterogeneous Particle Sizes, (Such as Soil in Wetland Areas, Sediment from Surface Water Bodies, or Organic Materials Such as Mulch or Peat):

Using a scoop, fill glass containers of sufficient size to accommodate the required sample mass and particle sizes as full as possible. Seal with PTFE-lined lids, place in ziplock bags, and place on ice in a cooler. The cooler is kept chilled at approximately 4EC and shipped with plenty of ice to the laboratory for receipt within 2 calendar days of sampling.

6.2.5 Sampling Oily Wastes:

Use an appropriate collection device based on the consistency of the waste and the container in which it is stored. Appropriate collection devices might include coliwassas, ladles, scoops, or spatulas. Collect two vials per sample location. Fill vials to minimize or eliminate headspace. Quickly seal vials.

Immediately upon capping, each filled vial is placed in a zip-lock bag and put on ice in a cooler. The cooler is kept chilled at approximately 4EC and shipped with plenty of ice to the laboratory for receipt within 2 calendar days of sampling.

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<sup>26</sup>En Novative Technologies, Inc., ibid.

### 6.3 Sample handling and shipment

All samples for volatiles analysis should be placed in zip-lock bags and put on ice in a cooler. The cooler should be kept chilled at approximately 4EC and shipped with plenty of ice to the laboratory for receipt within 2 calendar days of sampling. Shipment to the lab, and analysis after reaching the lab, should be carried out **as soon as possible**.

### 6.4 Sample storage

- 6.4.1 For Options 1a and 2a: Receipt at the Laboratory Within 2 Calendar Days of Sampling; Analysis Within 1 Additional Calendar Day\*: Once in the laboratory, store samples at 4EC until analysis. The sample storage area should be free of organic solvent vapors.

*\*Note: Samples **known to be high concentration** may be methanol preserved at this point instead of immediately analyzed. Methanol preservation must take place within 1 day of receipt. Once methanol preserved, extracts may be held up to 14 days at 4EC prior to analysis*

- 6.4.2 For Options 1b and 2b: Receipt at the Laboratory Within 2 Calendar Days of Sampling; Freezing Within 1 Additional Calendar Day\*: Once in the laboratory, store samples in a freezer at  $-12 \pm 3$ EC until shortly before analysis. Before analysis, bring samples to ambient temperature. The storage area should be free of organic solvent vapors.

*\*Note: Samples **known to be high concentration** may be methanol preserved at this point instead of frozen. Methanol preservation must take place within 1 day of receipt. Once methanol preserved, extracts may be held up to 14 days at 4EC prior to analysis.*

- 6.4.3 **All samples should be analyzed as soon as practical, and within the designated holding time from collection.** Samples not analyzed within the designated holding time must be noted and the data are considered minimum values.

## 7.0 PROCEDURE

This section describes procedures for sample screening and the low concentration soil method and high concentration soil methods for each sample collection option. It also provides a procedure for oily waste samples. The specific preparation and analysis procedures to be used for each sample depend on the expected concentration range:

- C Low concentration samples are run by closed system direct purge-and-trap using reagent water to aid in vapor partitioning as directed in **Section 7.2**. If results are to be reported on a dry weight basis, the dry weight procedure is also performed, as directed in **Section 7.5**.

- C High concentration samples are extracted with methanol (or another water-miscible solvent) as directed in **Section 7.3**. Following preparation they are introduced into the GC system using **SW-846 Method 5030**, “Purge-and-Trap for Aqueous Samples” or **SW-846 Method 5021**, “Equilibrium Headspace Analysis,” (or equivalent). In addition, the dry weight procedure is also performed, as directed in **Section 7.5**.
- C Oily waste samples that are soluble in water-miscible solvents are diluted with methanol or PEG as directed in **Section 7.4**, then purged using **SW-846 Method 5030** or **SW-846 Method 5021** (or equivalent).
- C Oily waste samples that are *not* soluble in water miscible solvents are diluted with n-hexadecane (or another suitable solvent) using **SW-846 Method 3585** “Waste Dilution for Volatile Organics.” They are then introduced to the GC system by direct injection.

## 7.1 Optional Screening

- 7.1.1 Reason for Screening: If the approximate concentration range for a sampling location is unknown, it is highly recommended that one collocated sample aliquot is screened for concentration prior to running the determinative purge-and-trap GC or GC/MS analysis. Samples may contain higher than expected quantities of purgeable organics that will contaminate the purge-and-trap system, thereby requiring extensive cleanup and instrument maintenance.
- 7.1.2 Screening Techniques: One collocated aliquot (one sample plug) is extracted with a solvent specified by the screening method to be used, such as methanol or n-hexadecane. The analyst may use any appropriate screening technique. Two suggested screening techniques using SW-846 methods include:
  - 7.1.2.1 *Method 5021*: Automated headspace using a gas chromatograph equipped with a photoionization detector (PID) and an electrolytic conductivity detector (HECD) in series, or
  - 7.1.2.2 *Method 3820*: Extraction of the sample with n-hexadecane and analysis of the extract on a GC equipped with a flame ionization detector (FID) and/or an electron capture detector (ECD).
- 7.1.3 Estimation of Upper Limit of Low Concentration Soil Method for Screening Purposes: The analyst may inject a calibration standard containing the analytes of interest at a concentration equivalent to the upper limit of the calibration range of the low concentration soil method. The results from this standard may be used to determine when the screening results approach the upper limit of the low concentration soil method. There are no linearity or other performance criteria associated with the running such a standard for to aid interpretation of screening results. Other approaches may also be used to estimate sample concentrations.

- 7.1.4 Results of Screening: Use the low concentration closed-system purge-and-trap method (Section 7.2) if the estimated concentration from the screening procedure falls within the calibration range of the selected determinative method. If the concentration exceeds the calibration range of the low concentration soil method, then use either the high concentration soil method (Section 7.3), or the oily waste method (Section 7.4) depending on sample solubility characteristics.

## 7.2 Low Concentration Soil Method

The concentration range applicable to the low level soil method is approximately 0.5 to 200 µg/kg. The actual concentration range that will be achieved in practice is dependent on the determinative method used and the sensitivity of each analyte.

### 7.2.1 Initial calibration

Prior to using this introduction technique for any GC or GC/MS method, the system must be calibrated. Refer to SW-846 Method 8000, "Determinative Chromatographic Separations," for a general discussion of calibration procedures. Refer to the determinative GC or GC/MS method and SW-846 Method 5000, "Sample Preparation for Volatile Organic Compounds," for specific information on calibration and preparation of standards. Normally, external standard calibration is preferred for the GC methods (non-MS detection) because of possible interference problems with internal standards. If interferences are not a problem, or when a GC/MS method is used, internal standard calibration may be employed. If a GC/MS method is selected, the instrument must be hardware-tuned according to the instrument manufacturer's recommendations prior to calibration.

7.2.1.1 *Assemble a purge-and-trap device* that meets the specification in Sec. 4.2 and that is connected to a gas chromatograph or a gas chromatograph/mass spectrometer system.

7.2.1.2 *Trap conditioning*: Before initial use, the trap should be conditioned overnight following the manufacturer's recommendations. During initial conditioning, the trap effluent should be vented to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes following the manufacturer's recommendations. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples. Instructions for conditioning traps described in EPA methods are provided below:

A. *If the Carbopack/Carbosieve trap described in Section 4.2.2.1 is used*, conditioning should be as follows:

- i.) Initial conditioning: Condition overnight at 245EC by back flushing with an inert gas flow of at least 20 mL/minute, venting to the hood.
  - ii.) Daily conditioning: Prior to daily use, the trap should be conditioned for 10 minutes at 245EC with back flushing, venting to the hood. Alternatively, the trap may be vented to the analytical column; however, the column must be run through the temperature program prior to analysis of samples.
- A. *If the standard trap described in Sec. 4.2.2.2 is used, condition as follows:*
- i.) Initial conditioning: Condition overnight at 180EC by back flushing with an inert gas flow of at least 20 mL/min (or according to the manufacturer's recommendations). Vent the trap effluent to the hood, not to the analytical column.
  - ii.) Daily conditioning: Prior to daily use, the trap should be conditioned for 10 min at 180EC with back flushing, venting to the hood. Alternatively, the trap may be vented to the analytical column; however, the column must be run through the temperature program prior to analysis of samples.

7.2.1.3 *Establish the purge-and-trap instrument operating conditions.*

- C. If the purge-and-trap system being used has the capability to add organic-free reagent water to the samples adjust the instrument to inject 5 mL of water.
- D. Adjust the instrument to heat the sample to 40EC, and to hold the sample at 40EC for 1.5 minutes before commencing the purge process, or as recommended by the instrument manufacturer.

7.2.1.4 *Calibration Standards*: Prepare a minimum of five initial calibration standards containing all the analytes of interest and surrogates, as described in SW-846 Method 8000, and following the instrument manufacturer's instructions. The calibration standards are prepared in organic-free reagent water. The volume of organic-free reagent water used for calibration must be the same volume used for sample analysis. The internal standard solution must be added in the same fashion as used for the samples (automatically by the instrument, or manually through the septum of the unopened vial).

7.2.1.5 *Purge calibration standards*: Place the soil vials containing the calibration standard solutions in the instrument carousel. Prior to purging each concentration standard, heat the vial to 40EC for 1.5 minutes, or as recommended by the manufacturer. Carry out the purge-and-trap procedure as outlined in Sections 7.2.3. to 7.2.5.

- 7.2.1.6 *Calculate calibration factors (CF) or response factors (RF) for each analyte of interest using the procedures described in SW-846 Method 8000. Calculate the average CF (external standards) or RF (internal standards) for each compound, as described in Method 8000. Evaluate the linearity of the calibration data, or choose another calibration model, as described in Method 8000 and the specific determinative method.*
- 7.2.17 *Pre-analysis system performance check: A system performance check must be made before the calibration curve is used to analyze samples. This procedure checks for proper purge flow and whether contaminated lines or active sites in the system have caused degradation. The performance check involves evaluating instrument response for the following four compounds: chloromethane; 1,1-dichloroethane; bromoform; and 1,1,2,2-tetrachloroethane.*
- A. *If a GC/MS determinative analysis will be used, see the evaluation criteria in the determinative method. For SW-846 Method 8260B, this information can be found in Section 7.3.5.*
  - B. *If a GC determinative analysis, such as SW-846 Method 8021 will be run, use the following information to evaluate the compounds' responses:*
  - C. *Chloromethane is the most likely compound to be lost if the purge flow is too fast.*
    - i.) *Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Also, cold spots and/or active sites in the transfer lines may adversely affect response.*
    - ii.) *Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.*
- 7.2.1.8 *High concentration, late eluting compounds: When analyzing for very late eluting compounds with SW-846 Method 8021 or similar GC methods, cross-contamination and memory effects from high concentration samples or standards are a common problem. Extra rinsing of the purge chamber after analysis normally corrects this. The newer purge-and-trap systems often overcome this problem with better bake out of the system following the purge-and-trap process. Also, the charcoal traps retain less moisture and decrease the problem. Examples of very late eluting compounds are 1,2,4-Trichlorobenzene; Hexachlorobutadiene; Naphthalene; and 1,2,3-Trichlorobenzene.*

## 7.2.2 Calibration Verification

Refer to SW-846 Method 8000B, Section 7.7, and to the determinative chromatographic method for details on calibration verification.

7.2.2.1 For GC analysis (non-MS detection), a single standard near the mid-point of the calibration range is used for verification.

7.2.2.2 For GC/MS analysis, calibration verification is a three-step process. Refer to SW-846 Method 8260B, Section 7.4, for detailed instructions.

## 7.2.3 Additional Sample Preparation When Sample Collection **Option 1** Has Been Used (Collection and Transportation in Coring Devices with Airtight Sample Chambers)

This section provides instructions for extrusion of samples from the En Core™ Sampler (or equivalent). If sample collection **Option 2** was used, proceed to Section 7.2.4.

7.2.3.1 Remove the sampler from storage (cooler or refrigerator) and allow to come to room temperature without removing cap.

7.2.3.2 Prepare soil vials (while wearing gloves):

- A. Label each vial with sample identification information.
- B. Add 5 mL organic-free reagent water to each vial.\*
- C. Attach the screw-cap and septum seal.
- D. Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

\*Note: Alternatively, sample plug can be extruded into a dry vial and the reagent water added later through the septum.

7.2.3.3 Extrude the soil into the vial<sup>27</sup> and obtain the sample weight:

- A. Wear gloves during all handling of pre-weighed vials. Remove cap and septum seal from vial.
- B. Rotate the locking arms on the cap of the En Core Sampler™ (or equivalent) to the flats on the locking ridge. Do not remove the cap at this time.
- C. Attach the En Core Sampler™ to the En Core Extrusion Tool:

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<sup>27</sup>En Novative Technologies, Inc. web page, “Disposable En Core™ Sample: Extrusion Procedures: Using the En Core™ Extrusion Tool,” <http://www.ennovativetech.com/instructions.htm>, p. 3 of 5.

- i.) Depress the locking lever on the Extrusion Tool.
- ii.) Place the Sampler, plunger end first, into the open end of the Extrusion Tool, *aligning the slots on the coring body with the pins in the Extrusion Tool*.
- iii.) Turn the coring body clockwise until it locks into place.
- iv.) Release the locking lever.
- D. Rotate and gently push the Extrusion Tool plunger knob clockwise until the plunger slides over the wings of the coring body. (When properly positioned, the plunger will not rotate further.)
- E. Hold the Extrusion Tool with the capped Sampler pointed upward so that no soil falls out when the cap is removed.
- F. Remove the cap from the Sampler and insert the end of the Sampler into a tared sample vial containing reagent water.
- G. Push the soil core into the VOA vial by pushing down on the plunger knob of the Extrusion Tool.
- H. Wipe any soil off the vial threads with paper toweling and cap the vial, hermetically sealing.
- I. Wipe off any soil on the exterior of the vial or cap.
- J. Weigh the vial and contents to the nearest 0.01 grams and record this weight.

7.2.3.4 *Proceed to Section 7.2.5.*

7.2.4 Additional Sample Preparation When Sample Collection **Option 2** Has Been Used (Empty VOA Vial)

7.2.4.1 *Obtain sample weight:* Weigh the vial and contents to the nearest 0.01 grams and record this weight.

7.2.4.2 *Add reagent water:* Without disturbing the hermetic seal on the sample vial, and using a syringe with a **narrow gauge needle (23-gauge or smaller)**, add 5 mL of organic-free reagent water to the vial through the septum. Shake the vial vigorously to disperse the sample before purging, and proceed to Section 7.2.5.

7.2.5 Sample Purge-and-Trap

This method is designed for a 5-g sample size, but smaller (or larger) sample sizes may be used. If purging a larger sample size to increase sensitivity, consult the instrument manufacturer's instructions regarding larger sample sizes, in order to avoid clogging of the purging apparatus. Adjust volume of reagent water as appropriate for sample size.

The soil vial was hermetically sealed at the sampling site (or at the lab after sample extrusion if sample collection Option 1 was used). The vial **MUST** remain hermetically sealed **THROUGHOUT** the preparation process in order to maintain the original concentrations of target analytes in the samples.

- 7.2.5.1 *Warming and Dispersion of Sample:* Remove the sample vial from storage and allow it to warm to room temperature. Shake the vial gently, to ensure that the contents move freely and that agitation during purging will be effective. Place the sample vial in the instrument carousel according to the manufacturer's instructions.
- 7.2.5.2 *Addition of Organic-Free Reagent Water, Surrogates, and Internal Standards:* Without disturbing the hermetic seal on the sample vial, add 5 mL of organic-free reagent water, the internal standards, and the surrogate compounds. Other volumes of organic-free reagent water may be used, however, it is imperative that all samples, blanks, and calibration standards have exactly the same final volume of organic-free reagent water.
- A. If the chromatographic system has an automated purge-and-trap system capable of adding reagent water solution containing surrogates and internal standards via a needle sparger, this can be done mechanically
- B. If an automated system is not available, the solution may be added manually through the septum using a syringe with a **narrow gauge needle (23 or smaller)**. The vial is not opened throughout the sample preparation and introduction process
- 7.2.5.3 *Addition of Matrix Spiking Solution:* For the sample selected for matrix spiking, add the matrix spiking solution described in Section 5.5 of SW-846 Method 5000, either manually, or automatically, following the manufacturer's instructions, and without disturbing the vial's hermetic seal. The concentration of the spiking solution and the amount added should be established as described in Section 8.5 of SW-846 Method 8000. If the spiking solution is added manually, it should be added with a narrow gauge needle (23 or smaller). A matrix spike (MS) and a matrix spike duplicate (MSD) should be prepared in this manner.
- 7.2.5.4 Prior to purging, heat the sample vial to 40EC for 1.5 minutes, or as described by the manufacturer.
- 7.2.5.5 Purge the sample with helium or another inert gas at a flow rate of up to 40 mL/minute (the flow rate may vary from 20 to 40 mL/min, depending on the target analyte group) for 11 minutes while the

sample is being agitated with the magnetic stirring bar or other mechanical means. The purged analytes are allowed to flow out of the vial through a glass-lined transfer line to a trap packed with suitable sorbent materials.

#### 7.2.6 Sample Desorption

The sample desorption process is dependent on whether or not the instrument has a cryogenic interface.

7.2.6.1 *Non-cryogenic interface:* After the 11 minute purge, place the purge-and-trap system in the desorb mode and preheat the trap to 245EC without a flow of desorption gas. Start the flow of desorption gas at 10 mL/minute for about four minutes (1.5 min is normally adequate for analytes in Method 8015). Begin the temperature program of the gas chromatograph and start data acquisition.

7.2.6.2 *Cryogenic interface:* After the 11 minute purge, place the purge-and-trap system in the desorb mode, make sure that the cryogenic interface is at -150EC or lower, and rapidly heat the trap to 245EC while back flushing with an inert gas at 4 mL/minute for about 5 minutes (1.5 min is normally adequate for analytes in Methods 8015). At the end of the 5-minute desorption cycle, rapidly heat the cryogenic trap to 250EC. Begin the temperature program of the gas chromatograph and start the data acquisition.

#### 7.2.7 Trap Reconditioning

After desorbing the sample for the requisite time (1.5 minutes for SW-846 Method 8015 and similar GC methods, 4 minutes for GC/MS instruments with non-cryogenic interface, or 5 minutes for GC/MS instruments with cryogenic interface), recondition the trap by returning the purge-and-trap system to the purge mode. Maintain the trap temperature at 245EC (or other temperature recommended by the manufacturer of the trap packing materials). After approximately 10 minutes, turn off the trap heater and halt the purge flow through the trap. When the trap is cool, the next sample can be analyzed.

#### 7.2.8 Data Interpretation

Perform qualitative and quantitative analysis following the guidance given in the determinative method and SW-846 Method 8000. If the concentration of any target analyte exceeds the calibration range of the instrument, it will be necessary to reanalyze the sample by the high concentration method. **Such reanalyses need only address those analytes for which the concentration exceeded the calibration range of the low concentration method.**

### 7.2.9 Determination of Dry Weight

If results are to be reported in dry weight, determine the dry weight of a separate aliquot of the sample, using the procedure in **Section 7.5**

### **7.3 High Concentration Method for Soil Samples with Concentrations Exceeding Linear Range of Low Concentration Calibration (Generally Greater than 200 µg/kg)**

The high concentration method for soil is based on a solvent extraction. A solid sample is either extracted or diluted, depending on sample solubility, in methanol or another water-miscible solvent.\*\* An aliquot of the extract is added to organic-free reagent water (containing internal standards and, for the MS and MSD aliquots, matrix spiking standards), and surrogates are added to the vial. The sample is then purged according to Method 5030 or introduced by equilibrium headspace according to Method 5021 (or equivalent) and analyzed by an appropriate determinative method. Wastes that are insoluble in methanol (such as petroleum and coke wastes) are diluted with n-hexadecane. (See Section 7.4.)

**\*\*Important Note:** Any free water present in the sample will be miscible with the extraction solvent and extracted along with the volatile analytes. This will volumetrically increase the extract phase, resulting in a dilution of the analytes extracted from the sample *and* a dilution of the surrogates, internal standards, and matrix spikes. **Calculations should be adjusted to account for this dilution.** The moisture content of the sample can be determined from the dry weight determination. Once the moisture content is known, results can be corrected by multiplying the “observed concentrations” (based on the volume of methanol alone) by the ratio:

$$\frac{\text{volume of methanol} + \text{water}}{\text{volume of methanol}}$$

The specific sample preparation steps depend on whether the sample was collected using sample collection **Option 1** or sample collection **Option 2**. Samples that were collected using **Option 1** are prepared using the steps below, beginning at Section 7.3.1. If **Option 2** was used, then the preparation begins with Section 7.3.3.

This method is designed for a 5-gram sample size, but other sample sizes may be used. If a sample size other than 5 grams is used, adjust methanol volume accordingly. The default ratio of sample to solvent is 1:1 (g:mL). I.e., if sample size is increased to 10 grams, methanol volume should be increased to 10 mL. The ratio may need to be adjusted because of sample characteristics (such as high organic content). See Section 7.3.2.2.

7.3.1 Additional Sample Preparation When Sample Collection **Option 1** Has Been Used (Collection and Transportation in Coring Devices with Airtight Sample Chambers)

This section provides instructions for extrusion of samples from the En Core™ Sampler (or equivalent). If sample collection **Option 2** was used, proceed to Section 7.3.3.

7.3.1.1 *Remove the En Core™ Sampler or equivalent device from storage (cooler or refrigerator) and allow to come to room temperature without removing cap.*

7.3.1.2 *Prepare soil vials (while wearing gloves):*

- A. Label each vial with sample identification information.
- B. Add 5 mL **methanol** to each vial.\*
- C. Attach the screw-cap and septum seal.
- D. Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

\*Note: Alternatively, sample plug can be extruded into a dry vial and the methanol added through the septum after sealing.

7.3.1.3 *Extrude the soil into the vial and obtain the sample weight:*<sup>28</sup>

- A. Wear gloves during all handling of pre-weighed vials. Remove cap and septum seal from vial.
- B. Rotate the locking arms on the cap of the En Core Sampler™ (or equivalent) to the flats on the locking ridge. Do not remove the cap at this time.
- C. Attach the En Core Sampler™ to the En Core Extrusion Tool:
  - i.) Depress the locking lever on the Extrusion Tool.
  - ii.) Place the Sampler, plunger end first, into the open end of the Extrusion Tool, *aligning the slots on the coring body with the pins in the Extrusion Tool.*
  - iii.) Turn the coring body clockwise until it locks into place.
  - iv.) Release the locking lever.
- D. Rotate and gently push the Extrusion Tool plunger knob clockwise until the plunger slides over the wings of the coring body. (When properly positioned, the plunger will not rotate further.)

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<sup>28</sup>En Novative Technologies, Inc. web page, "Disposable En Core™ Sampler: Extrusion Procedures: Using the En Core™ Extrusion Tool," <http://www.ennovativetech.com/instructions.htm>, p. 3 of 5.

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- E. Hold the Extrusion tool with the capped Sampler pointed upward so no soil falls out when the cap is removed.
- F. Remove the cap from the Sampler and insert the end of the Sampler into a tared sample vial containing reagent water.
- G. Push the soil core into the VOA vial by pushing down on the plunger knob of the Extrusion Tool.
- H. Wipe any soil off the vial threads with paper toweling and cap the vial, hermetically sealing.
- I. Wipe off any soil on the exterior of the vial or cap
- J. Weigh the vial and contents to the nearest 0.01 grams and record this weight.

7.3.1.4 Disperse the sample in methanol by gently swirling the vial so that the majority of the inner glass surfaces are rinsed.

7.3.1.5 Solvent ratio adjustment for matrix characteristics: If the 5 mL of methanol does not cover all of the soil, or if the soil expands to soak up all the free methanol, add an additional 5 mL of methanol.

**A. Record that 10 mL of methanol were used instead of 5 mL.**

**B. The analyst must account for the actual soil to solvent ratio in all calculations.\*\***

**\*\*Important Note:** Any free water present in the sample will be miscible with the methanol and extracted along with the volatile analytes. This will volumetrically increase the extract phase, resulting in a dilution of the analytes extracted from the sample *and* a dilution of the surrogates, internal standards, and matrix spikes. Calculations should be adjusted to account for this dilution. The moisture content of the sample can be determined from the dry weight determination. Once the moisture content is known, results can be corrected by multiplying the “observed concentrations” (based on the volume of methanol alone) by the ratio:

$$\frac{\text{volume of methanol} + \text{water}}{\text{volume of methanol}}$$

7.3.1.6 *Proceed to Section 7.3.3.*

### 7.3.2 Additional Sample Preparation When Sample Collection **Option 2** Has Been Used (Empty VOA Vial)

7.3.2.1 *Obtain Sample Weight:* Weigh the vial and contents to the nearest 0.01 grams and record this weight.

7.3.2.2 *Add Methanol and Disperse Sample:* Without disturbing the hermetic seal on the sample vial, and using a syringe with a **narrow gauge needle (23-gauge or smaller)**, add 5 mL of methanol to the vial through the septum to begin extracting the soil sample. Gently disperse the sample by swirling the vial so that the majority of the inner glass surfaces are rinsed.

- A. Solvent ratio adjustment for matrix characteristics: If the 5 mL of methanol does not cover all of the soil, or if the soil expands to soak up all the free methanol, add an additional 5 mL of methanol. **Record that 10 mL of methanol were used instead of 5 mL.**
- B. The analyst must account for the actual soil to solvent ratio in all calculations.\*\*

**\*\*Important Note:** Any free water present in the sample will be miscible with the methanol and extracted along with the volatile analytes. This will volumetrically increase the extract phase, resulting in a dilution of the analytes extracted from the sample *and* a dilution of the surrogates, internal standards, and matrix spikes. Calculations should be adjusted to account for this dilution. The moisture content of the sample can be determined from the dry weight determination. Once the moisture content is known, results can be corrected by multiplying the “observed concentrations” (based on the volume of methanol alone) by the ratio:

$$\frac{\text{volume of methanol} + \text{water}}{\text{volume of methanol}}$$

### 7.3.3 Add Surrogates and Extract Sample

7.3.3.1 *Add the surrogate spiking solution* to the vial by injecting it through the septum. Shake the vial for 2 minutes to mix surrogates with sample dispersed in methanol.

7.3.3.2 *Extract sample* by sonicating for 20 minutes.\* Allow sediment to settle until a layer of methanol is evident.

*\*Note: Alternatively, extraction may be accomplished by allowing samples to sit for 24 hours after shaking for 2 minutes.*

#### 7.3.4 Obtain Extract Aliquot and Prepare Blank

Using a syringe, withdraw 1 to 2 mL of the extract prepared in Section 7.3.3 from the soil sample vial and transfer to a GC vial for storage. Seal the vial. The remainder of the extract may be discarded. Add 1 to 2 mL of methanol from the same lot to a separate GC vial for use as the method blank for each set of samples extracted with that same solvent.

#### 7.3.5 Storage of High Concentration Methanol Extracts

The extracts must be stored at 4EC in the dark, prior to analysis.

#### 7.3.6 Prepare Sample Extracts for Analysis

If purge-and-trap will be performed, add an appropriate aliquot of the extract (see Table 2) to 5.0 mL of organic-free reagent water and analyze by SW-846 Method 5030 in conjunction with the appropriate determinative method. Proceed to Section 7.0 in Method 5030 and follow the procedure for high concentration samples.

Alternatively, if equilibrium headspace analysis will be performed by SW-846 Method 5021, withdraw 10 µL, or appropriate volume of extract (see Table 2) and inject into a 22 mL vial containing 10.0 mL of matrix modifying solution and internal standards (if required) and surrogates. Analyze by the headspace procedure by placing the vial into the autosampler and proceeding with Sec. 7.4.2.4. of SW-846 Method 5021.

#### 7.3.7 Determination of Dry Weight

Determine the dry weight of a separate aliquot of the sample, using the procedure in **Section 7.5**, after the sample extract has been transferred to a GC vial and the vial sealed.

### **7.4 High Concentration Method for Oily Waste Samples**

This procedure for the analysis of oily waste samples involves the dilution of the sample in solvent. However, care must be taken to avoid introducing any of the floating oil layer into the instrument. If soluble in a water-miscible solvent, a portion of the diluted sample is further prepared according to SW-846 Method 5030 or SW-846 Method 5021 (or equivalent), and analyzed using an appropriate determinative method.

The specific sample preparation steps depend on the solubility characteristics of the waste. If the oily sample is soluble in methanol or PEG, proceed to Section 7.4.2.

For oily samples that are not soluble in methanol or PEG (including those samples consisting primarily of petroleum or coking waste), dilute or extract with n-hexadecane using the procedures in Section 7.0 of SW-846 Method 3585. If the solubility of the sample is unknown, perform the solubility test described in Section 7.4.1, below, before proceeding.

#### 7.4.1 Solubility Test for Unknown Waste Samples

Remove several grams of material from the sample container. Quickly reseal the container to minimize the loss of volatiles. Weigh 1-g aliquots of the sample into several test tubes or other suitable containers. Add 10 mL of methanol to the first tube, 10 mL of PEG to the second, and 10 mL of hexadecane to the third. Swirl the sample and determine if it is soluble in the solvent. Once the solubility has been evaluated, discard these test solutions. If the sample is soluble in either methanol or PEG, proceed with Section 7.4.2. If the sample is only soluble in hexadecane, proceed with Section 7.4.8.

#### 7.4.2 Dilution Procedure for Oily Waste Samples Soluble in Methanol or PEG

For oily waste samples that are soluble in methanol or PEG, weigh 1 gram (wet weight) of the sample into a tared 10-mL volumetric flask, a tared scintillation vial, or a tared culture tube. If a vial or tube is used instead of a volumetric flask, it must be calibrated prior to use. This operation must be performed prior to opening the sample vial and weighing out the aliquot for analysis.

7.4.2.1 *To calibrate the vessel*, pipet 10.0 mL of methanol or PEG into the vial or tube and mark the bottom of the meniscus. Discard this solvent, and proceed with weighing out the 1-g sample aliquot into the vessel.

#### 7.4.3 Add Surrogates, Dilute with Solvent, and Disperse Sample

Quickly add 1.0 mL of surrogate spiking solution to the flask, vial, or tube, and dilute to 10.0 mL with the appropriate solvent (methanol or PEG). Swirl the vial to mix the contents and then shake vigorously for 2 minutes.

#### 7.4.4 Procedure for Addressing a Floating Oil Layer

The target analytes are extracted into the solvent along with the majority of the oily waste. However, some of the oily waste may still be floating on the surface. If oil is floating on the surface, transfer 1 to 2 mL of the extract to a clean GC vial using a Pasteur pipet. Ensure that no oil is transferred to the vial.

#### 7.4.5 Prepare Extract for Analysis

Add 10 - 50 µL of the methanol extract to 5 mL of organic-free reagent water for purge-and-trap analysis, using Method 5030.

Alternatively, if equilibrium headspace analysis by Method 5021 (or equivalent) will be performed, inject 10 µL (or appropriate volume of extract from Table 2) into a 22 mL vial containing 10.0 mL of matrix modifying solution, internal standards (if required) and surrogates. Place the vial into the autosampler and proceeding with Sec. 7.4.2.4. of Method 5021.

#### 7.4.6 Prepare Matrix Spike (and Matrix Spike Duplicate, if Applicable)

Prepare a matrix spike sample by adding 10 - 50 µL of the matrix spike standard dissolved in methanol to a 1-gram aliquot of the oily waste. Shake the vial to disperse the matrix spike solution throughout the oil. Then add 10 mL of extraction solvent. If the Sampling and Analysis Plan also calls for a matrix spike duplicate to be analyzed (instead of a matrix duplicate), prepare a second 1-gram aliquot from the same waste sample in the same manner. Proceed with the extraction and analysis, as described in Secs. 7.4.2 - 7.4.5. Calculate the recovery of the spiked analytes as described in Method 8000. If the recovery is not within the acceptance limits for the application, use the hexadecane dilution technique in Sec. 7.0 of Method 3585.

#### 7.4.7 Dry Weight Determination is **Not** Made on Solid Wastes that Are Being Analyzed for Disposal Characterization.

If the oily waste is heavily contaminated **soil** related to a remediation project, determine dry weight as detailed in Section 7.5. **However, Wastes being characterized for disposal, should not be reported on a dry weight basis.** In this case the dry weight determination is used to find out the amount of water in the sample. This water will be extracted by the methanol along with the analytes of interest. The dry weight information provides a tool to assess the dilution effects this water has on surrogates and internal standards.

### 7.5 Determination of % Dry Weight

Dry weight determination must be performed, and results must be reported on a dry weight basis, on all (high level and low level) samples that are being analyzed for *remediation-related projects*.

Dry weight determination must also be performed on high level samples being characterized for *disposal purposes that will be extracted in methanol*. **However, Wastes being characterized for disposal, should not be reported on a dry weight basis.**

It is not necessary to perform a dry weight determination on low level samples being characterized for disposal purposes.

7.5.1 Results **must be reported** on a dry weight basis for samples being analyzed for the following types of projects:

- Site assessments (of any type, for any program);
- Risk assessments (of any type, for any program);
- Resource Conservation and Recovery Act (RCRA) closures;
- RCRA Corrective Action projects;
- Voluntary Remediation Plan (VRP) projects;
- State Cleanup projects;
- Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or “Superfund”) projects;
- Leaking Underground Storage Tank (LUST) projects; and
- Enforcement-driven cleanups.

7.5.2 Results **should not be reported** on a dry weight basis for the following types of samples, even if dry weight is determined:

- Excavated soils and sediments being characterized for disposal,
- Other special wastes and solid wastes being analyzed for waste classification,
- Other special wastes and solid wastes being characterized for disposal.

7.5.3 Preparation for Drying Procedure

The specific preparation steps depend on whether the dry weight aliquot was an additional 5-gram plug collected with a coring device, or whether it was collected in the “traditional” (bulk) manner.

7.5.1.1 If the sample was collected as a 5-gram plug with a coring device, transfer the entire plug into a tared crucible.

7.5.1.2 If the sample was collected in the “traditional” manner, weigh 5-10 g of the sample from the vial or jar into a tared crucible.

7.5.4 Drying Procedure and Calculation

Dry this aliquot overnight at 105EC. Allow to cool in a desiccator before weighing. Calculate the % dry weight as follows:

**WARNING:** The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

## 8.0 QUALITY CONTROL

### 8.1 General Guidance

Refer to SW-846 Chapter One for specific quality control procedures and SW-846 Method 5000 for sample preparation QC procedures. Also see SW-846 Method 8000 for general guidance on QC procedures for chromatographic analysis. Each laboratory should maintain a formal quality assurance program.

### 8.2 Method Blank

Before processing any samples, the analyst should demonstrate through the analysis of an organic-free reagent water method blank that all glassware and reagents are interference free. Each time a set of samples is analyzed, or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

### 8.3 Initial Demonstration of Proficiency

Each laboratory must demonstrate initial proficiency with each sample preparation option and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat this demonstration whenever new staff are trained or significant changes in instrumentation are made. See Sec. 8.0 of SW-846 Method 5000 and Sec. 8.0 of SW-846 Method 8000 for information on how to accomplish this demonstration.

### 8.4 Sample Quality Control for Preparation and Analysis

See Sec. 8.0 in SW-846 Method 5000 and Sec. 8.0 in SW-846 Method 8000 for procedures to follow to demonstrate acceptable continuing performance on each set of samples to be analyzed. These include the addition of surrogates and internal standards to each sample and QC sample. In addition, each sample preparation batch of 20 or less samples should include a method blank, either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis, and a laboratory control sample (LCS). For low concentration samples a matrix spike duplicate analysis is preferred over a matrix duplicate.

### 8.5 Additional QA/QC Recommended

It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

## 9.0 METHOD PERFORMANCE

Accuracy and precision have not been specifically evaluated for Method IN 5035-M. The sample collection and storage options presented are modifications of SW-846 Method 5035 (December 1996) based on the studies, standards, and methods referenced. Please refer to the method performance sections in SW-846 Method 5035 and the other referenced documents for an approximation of IN 5035-M performance.

**Any questions regarding this policy should be directed to Mr. David Harrison of the Office of Land Quality at 317-232-8877. The IDEM toll-free telephone number is 1-800-451-6027.**

## 10.0 REFERENCES

1. American Society for Testing and Materials, ASTM D 4547-98, "Standard Guide for Sampling Waste and Soils for Volatile Organic Compounds," November 1998. (Current edition approved September 10, 1998 and published November 1998. Originally published as D 4547-91; last previous edition D 4547-91.)
2. En Novative Technologies, Inc. web page, "Disposable En Core™ Sample: Extrusion Procedures: Using the En Core™ Extrusion Tool," <http://www.ennovativetech.com/instructions.htm>
3. En Novative Technologies, Inc. Frequently Asked Questions (FAQ). Green Bay, WI: En Novative Technologies, 1998. Photocopy.
4. En Novative Technologies, Inc. SW 846 Method 5035 Field Sampling Guide, "En Core™ Sampler Collection for Low Level Analyses (\$1 Fg/kg)." Green Bay, WI: En Novative Technologies, 1998. Photocopy.
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6. IDEM, Office of Solid and Hazardous Waste Management, Technical Waste Assessment Section. "Freezing Preservation Issue Paper." Indianapolis: IDEM, July 1999.
7. IDEM, Office of Solid and Hazardous Waste Management, Technical Waste Assessment Section. *Guidance to the Performance and Presentation of Analytical Chemistry Data*, Appendix IV. Indianapolis: IDEM, July 1998.
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9. Turriff, David, and Chris Reitmeyer, *Validation of Holding Times for the En Core™ Sampler*. Green Bay, WI: En Novative Technologies, August 1998.
10. U.S. Environmental Protection Agency, *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*, SW-846, Third Edition, Final Update III. Methods 5000, 5030B, 5021, 5035, 8000B, and 8260B. December 1996.
11. U.S. Oil, U.S. Analytical Laboratory. "How to Collect Soil Samples with the EASYDRAW SYRINGE & The POWERSTOP HANDLE." U.S. Oil website: <http://www.usoil.com/uslab/lab/stepsmain.html>, 1998.

Table 1<sup>29</sup>**Some Typical Values for Different Densities OF Some Common Soil Materials\***

Soil Type	Density (g/cm <sup>3</sup> )		
	Saturated Density, $D_{sat}$	Dry Density, $D_{dry}$	Buoyant Density, $D'$
Sands and gravels	1.9 - 2.4	1.5 - 2.3	1.0 - 1.3
	1.4 - 2.1	0.6 - 1.8	0.4 - 1.1
Silts and clays	2.1 - 2.4	1.7 - 2.3	1.1 - 1.4
Glacial tills	1.9 - 2.2	1.5 - 2.0	0.9 - 1.2
Crushed rock	1.0 - 1.1	0.1 - 0.3	0.0 - 0.1
Peat	1.3 - 1.8	0.5 - 1.5	0.3 - 0.8
Organic Silts and clays			

\*Modified after Hansbo (1975).

Table 2

**Quantity of Methanol Extract Required for Analysis of High Concentration Soil/Sediment**

Approximate Concentration Range	Volume of Methanol Extract <sup>a</sup>
500 - 10,000 $\mu\text{g/kg}$	100 $\mu\text{L}$
1,000 - 20,000 $\mu\text{g/kg}$	50 $\mu\text{L}$
5,000 - 100,000 $\mu\text{g/kg}$	10 $\mu\text{L}$
25,000 - 500,000 $\mu\text{g/kg}$	100 $\mu\text{L}$ of 1/50 dilution <sup>b</sup>

Calculate appropriate dilution factor for concentrations exceeding those in this table.

- <sup>a</sup> The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of methanol is necessary to maintain a total volume of 100  $\mu\text{L}$  of methanol.
- <sup>b</sup> Dilute an aliquot of the methanol extract and then take 100  $\mu\text{L}$  for analysis.

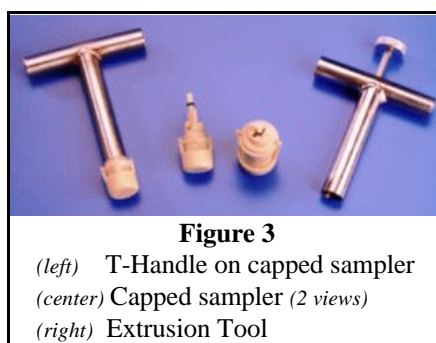
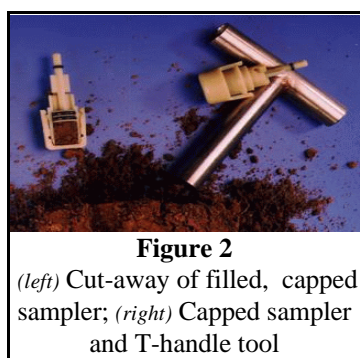
<sup>29</sup>Robert D. Holtz and William D. Kovacs, *An Introduction to Geotechnical Engineering*, (Englewood Cliffs, New Jersey: Prentice Hall, 1981), Table 2-1, p. 15.

## ISSUE PAPER: Field Sampling Equipment: Coring Devices for Collecting Cohesive but Uncemented Soils and Wastes (including tight clays)

This paper describes coring devices appropriate for use in Method IN 5035-M. Sources are provided for commercially available samplers.

12. *En Core™ Sampler:*\*\*\*\*\* (En Novative Technologies, Inc., 1241 Bellevue Street, Green Bay, WI 54302; Phone: (888) 411-0757; Fax: (920) 465-3963; e-mail: [info@ennovativetech.com](mailto:info@ennovativetech.com)), or equivalent.
  - ii The En Core™ Sampler is a disposable, semi-volumetric sampling device designed to collect, store and deliver intact soil samples with minimal handling and minimal exposure to atmosphere. It consists of three sections constructed of inert composite polymer: a coring body/sample chamber, a plunger, and a cap. A reusable T-handle is used to push the sampler into the soil, obtaining a headspace-free plug. The coring body is then sealed with the cap. O-rings in the coring body assembly and cap create an airtight seal, preventing exposure to the atmosphere until the sample is preserved or analyzed. Once at the laboratory, a reusable Extrusion Tool pushes the intact plug from the sampler into a volatile organic analysis (VOA) vial. Samplers are available in a 5-gram size and a 25-gram size. In general, the 5-gram size will be used for IN 5035-M.
  - ii This device may be used for collection, transportation, and storage as described in **Option 1**. (See Figures 1 and 2.) The En Core™ Sampler is currently the only combination coring/storage device approved by IDEM for **Option 1** of IN 5035-M.

### En Core™ Sampler



(Source of Figures 1 and 2: "Sampling Procedures Using the En Core™ Sampler," En Novative website, <http://www.ennovativetech.com/instructions.htm> )

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\*\*\*\*\*The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an endorsement or exclusive recommendation for use by IDEM. The products cited in IN 5035-M represent those products: (a) of which IDEM had knowledge at the time the method was written and (b) for which IDEM had confidence based on review of studies performed using that equipment, EPA approval, or both. Equipment other than that listed may be used provided that the resulting method performance meets the project data quality objectives and has been documented as described in SW-846 Chapter Two, Section 2.1.

IN5035-M Attachment 1

2. *EasyDraw Syringe™ & Powerstop Handle™*:\*\*\*\*\* (U.S. Oil Company, Inc., Analytical Laboratory Services, 1090 Kennedy Avenue, Kimberley, WI 54136; Phone: (800) 490-4902; Fax: (920) 739-1738; e-mail: [laboratory@usoil.com](mailto:laboratory@usoil.com)), or equivalent.

- ii The EasyDraw Syringe™ component is a disposable, inert polypropylene soil syringe with a tapered end, allowing easy penetration of soil. One disposable syringe is used for each sampling location.
- ii The Powerstop Handle™ is a specially designed, reusable syringe holder. The Powerstop Handle™ has been recently redesigned to account for soil density in the delivery of approximately 5, 10, or 13 gram samples without insertion or removal of a strike plate. The handle now has seven slots in which the EasyDraw Syringe™ can be inserted in order to collect the required volume based on soil type:
  - (a) Three 5-gram positions labeled light, medium, and heavy (to correspond to low, medium, and high soil densities);
  - (b) Three 10-gram positions labeled light, medium, and heavy; and
  - (c) One 13-gram position.

In general, for IN 5035-M the appropriate 5-gram position will be used to collect all aliquots except those to be used for screening and dry weight. The 10-gram or 13-gram positions should be used for the screening and dry weight aliquots.

- A. Together the syringe and handle function similarly to a cut-off modified syringe, but the handle design and tapered end of syringe provide greater ease for penetration of soil. The multiple slots on the handle dispense with the trial and error necessary to determine the correct volume on a cut-off modified syringe.
- B. The EasyDraw Syringe™ and Powerstop Handle™ may be used as a coring device for collection prior to transfer to VOA vials as described in **Option 2**. They (*See Figure 3.*)

#### **EasyDraw Syringe™ & Powerstop Handle™**



**Figure 4**  
EasyDraw  
Syringe™  
& Powerstop  
Handle™

(Source of Figure 3: "How to Collect Soil Samples with the EasyDraw Syringe & the Powerstop Handle" U.S. Oil website, <http://www.usoil.com/uslab/lab/stepsmain.html> )

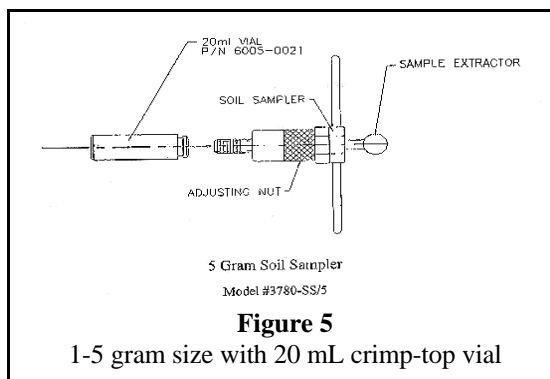
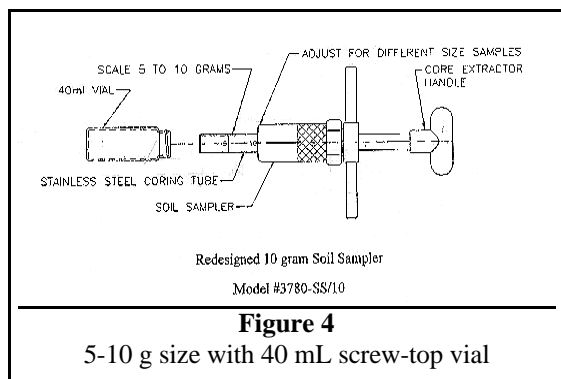
\*\*\*\*\*The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an endorsement or exclusive recommendation for use by IDEM. The products cited in IN 5035-M represent those products: (a) of which IDEM had knowledge at the time the method was written and (b) for which IDEM had confidence based on review of studies performed using that equipment, EPA approval, or both. Equipment other than that listed may be used provided that the resulting method performance meets the project data quality objectives and has been documented as described in SW-846 Chapter Two, Section 2.1.

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3. *Purge-and-Trap Soil Sampler™ - Model 3780-PT (3780-SS/10 and 3780-SS/5):* \*\*\*\*\* (Associated Design and Manufacturing Company, 814 North Henry Street, Alexandria, VA 22314; Phone: (800) 837-8257; Fax: (703) 548-0919), or equivalent.

- C. The Purge-and-Trap Soil Sampler™ is a reusable 1-piece stainless steel device with integrated handles. Two sizes are available. The 3780-SS/10 can be adjusted to deliver 5 to 10 gram samples. The coring end (stainless steel coring tube) fits into standard 40 mL VOA vials. The 3780-SS/5 can be adjusted to deliver 1 to 5 gram samples. The coring end fits into standard 20 mL crimp vials. Both sizes are designed to fine tune soil samples depending on loose or compact soil. Note: because the device (including coring tube) is reusable, it must be decontaminated between sampling locations.
- D. The Purge-and-Trap Soil Sampler™ may be used as a coring device for collection prior to transfer to VOA vials as described in **Option 2**. (Note: new design available as of 03/1999. See Figures 4 and 5.)

#### Purge-and- Trap Soil Sampler



(Source of Figures 3 and 4: Associated Design & Manufacturing Company, "New from Associated Design," March 1999, photocopy.)

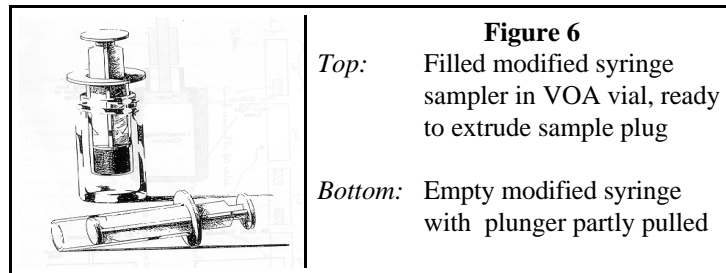
4. *Modified Syringe:* Samplers may inexpensively make their own coring devices from disposable plastic syringes. Disposable plastic syringes with a barrel smaller than the neck of the soil vial may be modified by cutting off the syringe end of the barrel and determining the volume required to obtain the required sample mass. (See Figure 6.)

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\*\*\*\*\* The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an endorsement or exclusive recommendation for use by IDEM. The products cited in IN 5035-M represent those products of which the agency had knowledge at the time the method was written. Equipment other than that listed may be used provided that the resulting method performance meets the project data quality objectives and has been documented as described in SW-846 Chapter Two, Section 2.1.

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- A. The modified syringe may be used as a coring device to collect aliquots prior to transfer to VOA vials as described in **Option 2**. Instructions for syringe modification are provided below:



(Source of Figure 4: ASTM D 4547-98, Fig. 3, "A Coring Tool Made by Cutting the Tip Off a Plastic Syringe," p. 6)

- A. One syringe is needed for each sample location and depth to be collected. The same syringe can be used to collect the multiple collocated aliquots at each location. Syringes can be discarded after use at one sampling location/depth. Alternatively, modified syringes can be decontaminated for reuse after all aliquots are collected at one sampling location/depth. There is no need to decon the syringe device between collocated aliquots at a single sampling location/depth.
- B. *Coring device preparation and estimate of soil volume for 5 grams:* The following preparations should be performed in a clean environment.
- E. Have at least 1 disposable 5- or 10-mL syringe per sampling location, plus a few extras. All the syringes used for a specific project should be the same size and type for ease in obtaining appropriate weight samples (through volume measurement).
- A. Cut off the "needle end" of the syringe barrel, thus creating a blunt, even coring end.
- B. Remove the rubber cap from the plunger.
- C. Determine the soil volume that will yield approximately 5-gram samples:
- (5) Using soil similar in type to the soil at the sampling site, collect several trial samples of varying length with the "extra" modified syringes.
  - (6) Weigh each trial sample on a top-loading balance and note the length of the soil column in the syringe.
  - (7) Use these data to determine the length of soil in the syringe that corresponds to  $5.0 \pm 0.5$  g. This length will be used for all samples collected on site.
  - (8) Discard the syringes used to determine sample length and the trial samples.

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**ISSUE PAPER: Freezing at  $-12 \pm 3\text{EC}$  as a Preservation Technique**

Indiana Modified Method 5035 (IN 5035-M) designates freezing soil samples in airtight containers at  $-12 \pm 3\text{EC}$  as the major method of preserving soil samples prior to analysis for volatile organic compounds (VOCs), if samples will not be analyzed on the date of receipt at the laboratory. Methanol preservation is allowed as an option for samples known to be high concentration (where there is prior knowledge that soils contain volatile organic compounds at concentrations exceeding the high end of the low concentration calibration curve). However freezing is encouraged even for high concentration samples.

*History of Freezing as Preservation for Volatiles in Soil*

The idea of freezing as an alternate preservation option was introduced in section 6.4.3 of Method 5035 for use with low-level calcareous soils that would effervesce upon addition of sodium bisulfate. No time limit or “holding time” for frozen samples was specified (SW-846 Final Update III, December 1996, p. 5035-12). The EPA memo, “Clarification Regarding Use of SW-846 Methods”,<sup>\*\*\*\*\*</sup> (hereinafter referred to as “Clarification Memo”), in its discussion of Method 5035 further suggests that freezing might be used as an alternative to analysis within 48 hours of sample collection. It states: “Longer holding times may be implemented if it can be conclusively demonstrated that alternative preservation techniques such as freezing samples. . . immediately upon receipt in the laboratory, does not compromise sample integrity.”<sup>\*\*\*\*\*</sup>

Since issuance of the “Clarification Memo,” holding time studies have been published in which VOA vials with 5-gram sample plugs and filled En Core™ Samplers were stored at  $-12 \pm 3\text{EC}$  for periods up to 12 days after receipt at the lab (following up to 2 days at  $4\text{EC}$ ). Both vials and samplers were included in the previously cited CRREL Special Report by Alan Hewitt, *Storage and Preservation of Soil Samples for Volatile Organic Compound Analysis* (January 1999). Frozen En Core™ Samplers were also covered in the En Novative Technologies report, *Validation of Holding Times for the En Core™ Sampler* (August 1998).

Data from both studies indicated significant slowing of VOC loss attributable to biodegradation and volatilization as compared to storage at  $4\text{EC}$ . However, there was some variation in results depending on specific volatile compound (molecular weight, aromatic versus halocarbon, etc.), soil type, and possibly type of storage chamber (sealed VOA vial versus sealed sampler). A recommendation has been submitted to the U.S. EPA to modify Method 5035 that would allow freezing at  $-12 \pm 3\text{EC}$  for 12 days (i.e., up to 14 days after sampling). That request is pending as of this writing.

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Memorandum to RCRA Senior Policy Analysts Region I-X, from Elizabeth Cotsworth, Environmental Protection Agency, Acting Director, Office of Solid Waste, “Clarification Regarding Use of SW-846 Methods” (Washington, D.C.: U.S. EPA, August 7, 1998), photocopy, Attachment 2, pp. 3-6.

<sup>\*\*\*\*\*</sup> Ibid., Attachment 2, p. 4.

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### *Indiana Decision on Holding Time at $-12 \pm 3EC$*

Because EPA has not yet issued definitive guidance on freezing soil samples for volatiles analysis, and because of the limited study data available and variation seen in the data generated in the two studies cited above, Indiana is reluctant to wholeheartedly endorse a 12-day freezing period at this time. Indiana is also aware that extensive losses from biodegradation (particularly for aromatic compounds) and/or volatilization (particularly for the lower molecular weight compounds and for sandy soil matrices) can and does occur in the 2 day period at 4EC allowed for transportation to the laboratory, even with careful handling. However, until such time as procedures have been established for freezing samples in the field immediately after collection, we see such losses as inevitable.

**After extensive review and discussion, Indiana has decided to set a holding time of 5 days at  $-12 \pm 3EC$  for freezing as preservation.** Together with the 2 days at 4EC allowed for transportation to the laboratory, this creates a total holding time of 7 days from the date of sampling. Based on the data available to date, we feel that this approach is a reasonable compromise between maximization of practicality for field staff and laboratories and maximization of measures to ensure data integrity.

Longer holding times at  $-12EC \pm 3EC$  will be allowed as a PBMS approach on a case-by-case basis if a demonstration is provided that the integrity of the samples will be maintained. The nature of and requirements for a satisfactory demonstration will depend on site-specific conditions, in particular analytes of concern and soil type.

### *Indiana Decision Against Chemical Preservation for Low Concentration Samples*

Freezing was selected as the preservation technique of choice because it eliminates many of the problems created when preservation is accomplished by chemical means. The following is a discussion of Indiana's reasoning in selecting freezing in preference of chemical preservation:

#### **Sodium Bisulfate Preservation**

SW-846 Method 5035 Requirements: SW-846 Method 5035 requires low concentration samples to be preserved in the field with sodium bisulfate solution. This is accomplished by taking tared VOA vials to the field that contain preservative solution and stirring bars. A 5-gram sample is extruded from a coring device directly into the bisulfate solution in the VOA vial; the vial is then sealed. Samplers are encouraged to calibrate a portable balance in the field and weigh the sealed vials to ensure that  $5.0 \pm 0.5$  grams have been collected. As an alternative to field preservation, SW-846 Method 5035 also allows low concentration samples to be collected in the En Core™ sampler for transportation to the laboratory where they must be analyzed or transferred to VOA vials containing bisulfate within 48 hours. Analysis of bisulfate-preserved samples requires blanks and standards to contain equivalent concentrations of bisulfate.

IDEM Decision Against Bisulfate Preservation - Associated Problems: Additional studies conducted after the release of SW-846 Method 5035 discovered the following complications related to the use of sodium bisulfate as a chemical preservative for soil VOCs. Because of these

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problems, Indiana elected to disallow sodium bisulfate preservation except as a PBMS approach.

- *Difficulties with Preservation in the Field:* A major reason for the creation of IN 5035-M is to move away from SW-846 Method 5035's procedures of adding reagents and performing weighings in the field:

(I) It is difficult to extrude soil plugs into vials containing preservative solutions without spillage. \*\*\*\*\* Spillage creates errors in sample weight leading to inaccurate quantification.

(J) It is awkward to work with a balance and difficult to obtain and maintain balance calibration in the field. \*\*\*\*\*

(xi) *Indiana Soils:* Indiana has calcareous soils in the southern portion of the state. Calcareous soils effervesce on contact with the acidic bisulfate solution, leading to the following problems:

1.1 Underestimated results caused by loss of VOCs to effervescence prior to capping vials.

1.2 Safety hazard: After the vials are capped, pressure may continue to build and shatter the glass.

- *Chemical Interactions between Sodium Bisulfate and Compounds in Samples and Standards:*

(A) Sodium bisulfate quickly degrades some compounds, notably styrene and 2-chloroethylvinyl ether, causing false negatives or biased low results in samples. \*\*\*\*\*

(A) The acidic condition created by sodium bisulfate oxidizes or decomposes naturally occurring compounds in soils with high humus content (such as carboxylic acids and alcohols) to acetone, causing false positives or biased high results. \*\*\*\*\*

(A) Standard solutions containing the bisulfate preservative degrade more rapidly over time than non-acidified standards, requiring more frequent monitoring and solution replacement. \*\*\*\*\*

## Methanol Preservation

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\*\*\*\*\*  
Rock J. Vitale, Ruth Forman, and Lester Dupes, "Comparison of VOC Results Between Methods 5030 and 5035 on a Large Multi-State Hydrocarbon Investigation," *Environmental Testing and Analysis* 8, no. 1 (January/February 1999): p. 36.

\*\*\*\*\*  
Ibid.

\*\*\*\*\*  
Jerry L. Parr, "Preservation Techniques and Holding Times for Soil Samples for Volatile Organics," (Evergreen, Colorado: Catalyst Information Resources, L.L.C., August 1998), p. 2; Alan D. Hewitt, "Enhanced Preservation of Volatile Organic Compounds in Soil with Sodium Bisulfate," CRREL Special Report 95-26, ([Hanover, New Hampshire]: U.S. Army Corps of Engineers CRREL, November 1995),

\*\*\*\*\*  
Alan D. Hewitt, *Storage and Preservation of Soil Samples for Volatile Compound Analysis*, (Hanover, New Hampshire: U.S. Army Corps of Engineers, Cold Regions Research & Engineering Laboratory, May 1999), 16, CRREL Special Report 99-5.

\*\*\*\*\*  
Telephone conversation with Chris Reitmeyer (En Novative Technologies, Inc.), February 1999.  
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Pros and Cons of Methanol Preservation: SW-846 Method 5035 specifies methanol preservation (either in the field or after receipt at the laboratory) for “high concentration” samples, defined in the Method as “generally greater than 200 Fg/kg.” SW-846 Method 5035 does not permit methanol preservation and extraction of low concentration samples because the use of methanol introduces a dilution factor that raises the sample quantitation limit beyond the operating range of the low level procedure. \*\*\*\*\* Other sources recommend the use of methanol for both low and high concentration samples on the basis that methanol extraction is a more robust procedure. The research of Alan Hewitt at the U.S. Army Corps of Engineers Cold Regions Research & Engineering Laboratory (CRREL) indicates that the methanol extraction procedure performed on replicate spikes exhibits “consistent accuracy despite inevitable variations in the sample matrix” and provides higher recoveries than vapor partitioning methods. \*\*\*\*\* Several states routinely require methanol preservation for soil VOC samples, including the Region 5 states of Michigan and Wisconsin. \*\*\*\*\* Emphasis is placed on immediate methanol preservation in the field.

Users of the methanol procedure for low level samples take steps to reduce the adverse effect of methanol on the quantitation limit. Examples include using no more than a 1:1 ratio of soil to methanol to minimize the dilution factor (e.g., 5 grams soil to 5 mL methanol) and performing the determinative analysis by a more sensitive GC method (such as SW-846 Method 8021) instead of a GC/MS method (such as SW-846 Method 8260). The Wisconsin Department of Natural Resources (WDNR) laboratory has found a quantitation limit of 25 Fg/kg to be reasonable for most compounds when analyzing methanol-preserved samples by a modified Method 8021 using electrolytic conductivity (ELCD) and photoionization (PID) detectors in series. Compounds can be detected at lower levels than this but quantitative accuracy deteriorates. However, WDNR also acknowledges that the low level calibration curve used in the quantitation limit study they performed is not typically used in “production” (i.e., commercial laboratory) settings. \*\*\*\*\* Laboratories generally consider methanol preservation/extraction to be a medium level technique. Quanterra, Inc. officers state that for commercial laboratories using the methanol preservation technique, “Typical reporting limits for most analytes are 0.5 Fg/g [500 Fg/kg] for gas

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\*\*\*\*\* U.S. Environmental Protection Agency, *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods*, SW-846, Third Edition, Final Update III. Method 5035, December 1996, pp. 5035-2, 5035-10.

\*\*\*\*\* Alan D. Hewitt, *Preparing Soil Samples for Volatile Organic Compound Analysis*, (Hanover, New Hampshire: U.S. Army Corps of Engineers, Cold Regions Research & Engineering Laboratory, April 1997), 15, CRREL Special Report 97-11; Alan D. Hewitt, “Comparison of Sample Preparation Methods for the Analysis of Volatile Organic Compounds in Soil Samples: Solvent Extraction vs. Vapor Partitioning,” *Environmental Science & Technology* 32, no. 1 (1998): pp. 143-149.

\*\*\*\*\* The Wisconsin Department of Natural Resources actively participated in the development of methanol preservation for soil VOCs for applications in the LUST program. See David Turriff and Chris Klopp, “Studies of Sampling, Storage and Analysis of Soils Contaminated with Gasoline and Diesel,” (WDNR, [1995]).

\*\*\*\*\* David Turriff and Chris Klopp, “Studies of Sampling, Storage and Analysis of Soils Contaminated with Gasoline and Diesel,” Doc. No. SW-513, (Madison: Wisconsin Department of Natural Resources, [1995]), pp. 20-21. Available on WDNR website: <http://www.dnr.state.wi.us/org/aw/rr/archives/pubs/SW513.pdf>

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chromatography/mass spectroscopy (GC/MS) and 0.05 Fg/g [50 Fg/kg] for GC methods.\*\*\*\*\*

IDEM Decision Against Methanol Preservation for **Low Concentration** Samples: After much study and discussion, it was decided that IN-5035 M would specify methanol preservation in the field only for difficult sample matrices (such as gravel). However, methanol preservation of soil samples known to be high concentration would be allowed at the laboratory in place of freezing. Other applications of the methanol procedure would be considered on a case-by-case basis as a PBMS approach. These decisions are based on the following reasons:

- (A) *Quantitation Limits and RISC Levels:* The use of methanol introduces a dilution factor that raises analyte quantitation limits. This introduces complications because most of the soil samples that will be analyzed for VOCs in Indiana will be used to obtain data for risk assessments or will be subject to Indiana's *Risk Integrated System of Closure (RISC)* criteria. The Tier 1 residential soil closure levels for two of the carcinogenic volatiles, benzene and vinyl chloride, are very low. Benzene will be a target analyte at most sites, including all Leaking Underground Storage Tank (LUST) sites. Vinyl chloride will be a target analyte (as a potential degradation product) at all sites for which tetrachloroethene (PCE), trichloroethene (TCE), or any of the dichloroethenes are target analytes. The default residential level for **benzene** is **34 Fg/kg** (0.034 mg/kg) and for **vinyl chloride** is **13 Fg/kg** (0.013 mg/kg).
1. 13 and 34 Fg/kg are lower than the typical commercial laboratory reporting limits in methanol of 50 Fg/kg for GC methods. They are even pushing the WDNR laboratory GC detection limit of 10 Fg/kg\*\*\*\*\* and quantitation limit of 25 Fg/kg (which require special care to obtain).
  2. Indiana labs typically analyze VOCs by standard GC/MS methods without modification. Typical commercial laboratory GC/MS reporting limiting limits in methanol are 500 Fg/kg, an order of magnitude higher than the RISC levels.
  3. Method development costs to obtain lower quantitation limits in methanol incurred by laboratories would be passed on to sample submitters.
- *Difficulties with Preservation in the Field:*
    - It is difficult to extrude soil plugs into vials containing preservative solutions without spillage.\*\*\*\*\* Spillage creates errors in sample weight leading to inaccurate quantification.

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\*\*\*\*\* Jerry L. Parr and Richard Burrows, "Issues in Sampling and Analysis of Volatile Organics in Soils," *Environmental Testing & Analysis* 7, no. 1 (January/February 1998): p. 28.

\*\*\*\*\* Turriff and Klopp, *ibid.*

\*\*\*\*\* Rock J. Vitale, Ruth Forman, and Lester Dupes, "Comparison of VOC Results Between Methods 5030 and 5035 on a Large Multi-State Hydrocarbon Investigation," *Environmental Testing and Analysis* 8, no. 1 (January/February 1999): p. 36.

- It is awkward to work with a balance in the field and very difficult to maintain calibration.  
\*\*\*\*\*
- Even if pre-measured ampules of methanol are added to the vial immediately after the sample plug (to eliminate methanol measurement in the field and potentially eliminate field weighings if a standard weight is assumed for the methanol), spillage could occur prior to capping, rendering the sample weight inaccurate.
- *Indiana Soils:* Many Indiana soils contain high organic and high clay content. When methanol is added to such soils, they tend to expand to soak up the methanol. This makes it impossible to obtain an aliquot of extract without adding more methanol. The increased volume of methanol, in turn, drives the sample quantitation limit even higher. Higher quantitation levels make it more difficult to determine regulatory, closure, or cleanup levels.

### *Future Considerations*

Research is continuing in the area of freezing as preservation. More data is being collected and evaluated for soil samples frozen in conventional freezers upon receipt at the laboratory. In addition, freezing samples in the field directly after collection through the use of dry ice and other means is also being studied. The U.S. EPA continues to evaluate the results of this research as it is received.

IN 5035-M may be modified in the future to reflect the continuing research results, guidance from the U.S. EPA, or the issue of a modification to SW-846 5035 (i.e., 5035A).

IN5035-M Attachment 2

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\*\*\*\*\*  
Ibid.